

# Copolymerization<sup>1</sup>

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A critical discussion of the mechanism of formation of copolymers by addition polymerization is presented. It deals mainly with the following three fundamental aspects: First, the quantitative treatment of the reaction starting with a scheme consisting of initiation, growth, and termination mechanisms. Expressions for the instantaneous and total copolymer composition and for the over-all rate of reaction as function of monomer composition and of conversion are derived in terms of quantities characteristic of the reaction. Graphical and numerical methods for the determination of these parameters from experimental data are given in detail. The statistical distribution of molecular weights and compositions in the product is considered in relation to the constants of the reaction and to the analogous case of simple polymers.

Second, methods for the analysis of copolymer compositions are discussed and experimental results are summarized. Reactivity ratios describing the behavior in growth of a given radical toward a pair of monomers are tabulated for a series of systems.

Third, these results are interpreted on the basis of resonance and of electrostatic and steric effects as encountered in the study of certain organic reactions.

In addition, degradation of copolymers is briefly considered in the light of the possible types of sequences in the chain. A numerical relation between yield and copolymer composition is derived.

The problems remaining are principally the following: Experimental methods of copolymer analysis, determination of over-all rates of reaction and of individual rate constants, and a more fundamental correlation between structure of monomers and behavior in copolymerization. Also, systematic data on the thermodynamic and rate properties of copolymer solutions should be of great interest, and studies of the bulk properties and their relation to copolymer structure represent a field where research has only recently been initiated.

## I. Introduction

Following the extensive experimental and theoretical attack on the general problem of chain polymerization reactions, recent years have brought a series of fundamental investigations regarding copolymerization reactions. A framework for the analysis of over-all monomer consumption and resulting change in average polymer composition has been created [1, 18, 26, 31]<sup>2</sup> and tested experimentally [5, 18]. Equations for the size and composition distributions have also been developed [26, 28]. However, no systematic experimental results on such distributions are avail-

able at present. Finally, interpretations of the differences in relative reactivities have been made on the basis of the electronic structure of the individual monomers [15, 24]. It is the purpose of this article to review the main points of these theoretical and experimental investigations. In respect to the former, stress will be laid on those aspects which also have been examined experimentally.

## II. List of Important Symbols

$A, B$	=respective numbers of monomer molecules of copolymerizing species. Also used to indicate species.
$A_0, B_0$	=initial values of $A$ and $B$ .
$z$	=ratio $A/B$ .
$z_0$	=initial value of $z$ .
$C$	=catalyst concentration.

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<sup>2</sup> Figures in brackets indicate the literature references at the end of this paper.

$n_{rs}(A)$	=number of radical chains with an active $A$ -end containing $r$ $A$ -units and $s$ $B$ -units.
$n_{rs}(B)$	=number of radical chains with an active $B$ -end, containing $r$ $A$ -units and $s$ $B$ -units.
$A^*$	=total number, $\sum_{r,s} n_{rs}(A)$ of radical chains with an active $A$ -end.
$B^*$	=total number, $\sum_{r,s} n_{rs}(B)$ of radical chains with an active $B$ -end.
$N_{rs}$	=number of stable polymer chains contain $r$ $A$ -units and $s$ $B$ -units.
$I_A$	=first order rate constant for initiation of monomer species $A$ .
$I_B$	=first order rate constant for initiation of monomer species $B$ .
$I$	=rate constant for production of radicals from catalyst.
$k_{gA}(A)$	=rate constant for propagation by addition of $A$ -monomer to a radical with an active $A$ -end.
$k_{gB}(A)$	=rate constant for propagation by addition of $B$ -monomer to a radical with an active $A$ -end.
$k_{gA}(B)$	=rate constant for propagation by addition of $A$ -monomer to a radical with an active $B$ -end.
$k_{gB}(B)$	=rate constant for propagation by addition of $B$ -monomer to a radical with an active $B$ -end.
$k_{gA}(r, s, A)$	=rate constant for propagation defined in the same manner as $k_{gA}(A)$ above, but dependent on composition $r, s$ of growing radical.
$k_t(A, A)$	=rate constant for mutual termination of two radicals with active $A$ -ends.
$k_t(A, B)$	=rate constant for mutual termination of two radicals with active $A$ - and $B$ -ends, respectively.
$k_t(B, B)$	=rate constant for mutual termination of two radicals with active $B$ -ends.
$\sigma$	=reactivity ratio $k_{gA}(A)/k_{gB}(A)$
$\mu$	=reactivity ratio $k_{gB}(B)/k_{gA}(B)$
$V_A + V_B$	=over-all rate of copolymerization per unit number of radicals.
$w_p$	=total weight of polymer at a given instant.
$w_0$	=initial weight of monomer.
$l$	=degree of polymerization of radical or stable polymer.
$y$	=composition deviation of individual chain from the mean.
$w(l, y)$	=distribution function of composition and chain length expressed as weight fraction in terms of above quantities $l$ and $y$ .
$\lambda$	=number of average degree of polymerization of radical chains.
$P_i(A)$	=probability of occurrence of $i$ $A$ -units in succession in a copolymer chain.
$P_i(B)$	=probability of occurrence of $i$ $B$ -units in succession in a copolymer chain.
$\omega(A)$	=probability of formation of an $A$ - $A$ linkage by propagation.

$\omega(B)$  =probability of formation of  $B$ - $B$  linkage by propagation.

### III. Quantitative Treatment

#### 1. General Remarks on Chain Polymerization Reactions

It is well established today that initiation, growth, and termination are the principal, although not necessarily the only mechanisms that determine the kinetics of chain polymerization reactions. The rates of these individual steps vary widely. The growth reaction is the fastest. The initiation, which produces, by one means or another, out of a stable monomer an activated radical is by far the slowest step, whenever long chains are formed. Otherwise, the supply of active monomer would be too large compared with the demand of the growth reaction for stable monomer.

The crucial step then, to begin with, is the production of a certain number of radicals able to grow before they are terminated. Their total concentration is determined by the initiation and termination only, since the growth merely changes their molecular weight. If they are terminated much faster than they are produced, an equilibrium is established. The exact condition for this to be true requires the mean life time of the active radicals to be small in comparison with that of stable monomer. This defines a quasistationary state and allows the expression of the "steady state" concentration of free radicals by means of an "equilibrium" constant given by the ratio

$$\text{Equilibrium constant} = \frac{\text{rate of production of free radicals}}{\text{rate of destruction of free radicals}}$$

This additional, and in most cases of interest, valid assumption simplifies considerably the quantitative treatment. It is then possible to develop completely the kinetics of the polymerization reaction and the resulting molecular size distribution [12] on the basis of a postulated reaction mechanism.

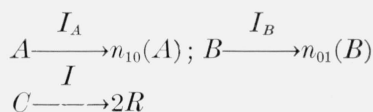
It will be shown here how to carry this program through when two or more competing monomer species are present. Additional problems then arise. One of the most important questions is concerned with the change in average polymer composition with changing composition of monomer residue. The mean composition depends on the relative rate with which the different

species enter the growing chain and hence, upon the relative growth rates, if we exclude the insignificant number of dimers, trimers, and other very short chains. In addition to the inhomogeneity in respect to chain length necessarily occurring in polymerizing systems, there will now exist also fluctuations of the composition from chain to chain. These fluctuations depend upon those in the long chain radicals. All three steps are essential for the determination of the distribution curves.

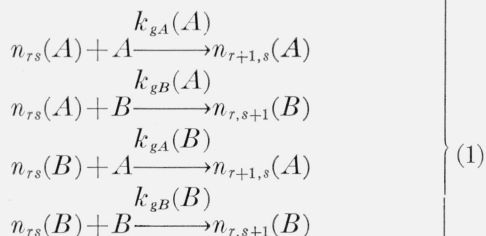
## 2. Basic Reaction Scheme and Equations

After these general remarks, we turn to the treatment of the copolymerization of a binary system, assuming the simplest possible reaction scheme, as indicated above. No kinetic studies exist at present that would necessitate the consideration of additional elementary acts, as is the case for one-component systems. In view of what was said previously this would not effect the calculation of average polymer compositions. In what follows, let  $n_{rs}(A)$  be the number of growing radical chains, each of which contains altogether  $r$  units of component  $A$  and  $s$  units of component  $B$ , while having an activated end consisting of an  $A$ -type monomer.  $n_{rs}(B)$  is then correspondingly defined.  $N_{rs}$  represents the number of stabilized chains of specified composition.  $C$  is a catalyst molecule and  $R$  a radical produced by its decomposition. The following scheme may then be considered.

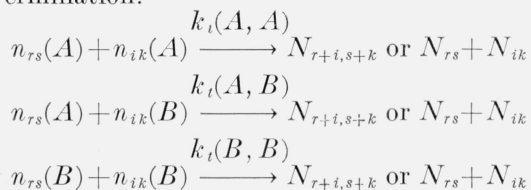
Initiation:



Growth:



Termination:



Copolymerization

In writing the initiation equation we have considered two types of activation. In the catalyzed activation the elementary act consists in a decomposition of the catalyst  $C$ . In the equations for growth and termination, we have differentiated between  $A$ - $A$ ,  $A$ - $B$ ,  $B$ - $A$ , and  $B$ - $B$  addition of monomer to radical and radical to radical, respectively. The rates of consumption of monomer are given according to eq 1 by

$$\begin{aligned} -\frac{1}{A} \frac{dA}{dt} &= I_A + k_{gA}(A) \sum_{r,s} n_{rs}(A) + k_{gA}(B) \sum_{r,s} n_{rs}(B) \\ -\frac{1}{B} \frac{dB}{dt} &= I_B + k_{gB}(A) \sum_{r,s} n_{rs}(A) + k_{gB}(B) \sum_{r,s} n_{rs}(B). \end{aligned} \quad (2)$$

The terms  $I_A$  and  $I_B$  are omitted for a catalyzed polymerization. Otherwise, they are small and can be neglected in comparison with the growth terms in eq 2. The summations are carried out over all values of  $r$  and  $s$ . The concentrations of free radicals  $\sum n_{rs}(A)$  and  $\sum n_{rs}(B)$  in a steady state obey the following relations if the initiation term is omitted:

$$\begin{aligned} \frac{d\sum n_{rs}(A)}{dt} &= k_{gA}(B)A \sum n_{rs}(B) - k_{gB}(A)B \sum n_{rs}(A) - \\ &\quad k_t(A,A) \sum n_{rs}(A) \sum n_{ik}(A) - \\ &\quad k_t(AB) \sum n_{rs}(A) \sum n_{ik}(B) = 0. \end{aligned} \quad (3)$$

An analogous equation results for  $\sum n_{rs}(B)$ . Equation 3 expresses the fact that  $A$ -type radicals are produced by addition of  $A$ -type monomer to  $B$ -type radicals, and they are destroyed by adding  $B$ -type monomer and by termination with an  $A$ - or  $B$ -type radical. The terms contributed by the chain-breaking reaction are small compared with the growth terms in eq 3, if long chains are to be formed. Hence, they may be neglected, and we obtain the simple relation:

$$\sum n_{rs}(A) = \frac{k_{gA}(B)A}{k_{gB}(A)B} \sum n_{rs}(B). \quad (3a)$$

It expresses the fact that free radicals with an active end  $A$  are produced as rapidly by addition of monomer  $A$  to free radicals with an active end  $B$  as they are destroyed by addition of monomer  $B$  to free radicals with an active end  $A$ .

## 3. Compositional Relationships: Average Composition, Relation to Conversion

Insertion of eq 3a into eq 3 leads to the following

relation for the change in composition of monomer residue:

$$\frac{dA}{dB} = \frac{A}{B} \frac{k_{gA}(B)}{k_{gB}(A)} \frac{k_{gA}(A)A + k_{gB}(A)B}{k_{gA}(B)A + k_{gB}(B)B} \quad (4)$$

It has been assumed in eq 1 that the rate constants are essentially independent of chain length, an assumption commonly made in chain polymerization reactions and shown to be true in polycondensation reactions [11].<sup>3</sup> Furthermore, they are independent of chain composition  $r, s$  in eq 1. Herington and Robertson [12] have established equations that allow in principle a deduction of such a dependence from molecular-weight distributions. Analogous relations for copolymerizing systems have been developed by Simha and Branson [26]. However, the equations are too complex and experimental results nonexistent to merit further discussion here. It may be noted only that eq 4 is unaffected by any such assumption. If the growth rates depend upon the composition, then the constants  $k_{gL}(M)$  in eq 4 represent mean values averaged over the radicals  $n_{rs}(M)$  with the particular end  $M$ , that is, for instance:

$$k_{gA}(A) = \frac{\sum k_{gA}(r, s, A) n_{rs}(A)}{\sum n_{rs}(A)}$$

$$k_{gA}(B) = \frac{\sum k_{gA}(r, s, B) n_{rs}(B)}{\sum n_{rs}(B)}$$

Equation 4 gives the relative rates of consumption of the two monomer species  $A$  and  $B$  under the approximations stated previously. It also represents the instantaneous average composition of copolymer formed at an instant in which the monomer residue consisted of  $A$  moles of species one and  $B$  moles of species two. This composition can not depend on the absolute magnitude of the growth rates  $k_g$  but only upon the relative rates of addition of each monomer species. Hence, the following parameters are defined [18:]

$$\left[ \frac{A+A}{A+B} \right] = \sigma = \frac{k_{gA}(A)}{k_{gB}(A)}, \quad \left[ \frac{B+B}{B+A} \right] = \mu = \frac{k_{gB}(B)}{k_{gA}(B)} \quad (5)$$

The symbols in the brackets indicate the modes of addition to which the constants  $\sigma$  and  $\mu$  refer.<sup>4</sup>

<sup>3</sup> H. W. Melville (lecture presented at the National Bureau of Standards on April 11, 1947) finds that growth and termination rates decrease but slightly with increasing chain length in the polymerization of vinyl acetate in the liquid phase.

<sup>4</sup> Various other symbols have been used for the ratios denoted here by  $\sigma$  and  $\mu$ , namely,  $1/\alpha, \beta$  [1],  $\sigma, \rho$  [3],  $\alpha, \beta$  [28],  $r_1, r_2$  (T. Alfrey, F. R. Mayo F., T. Wall, *J. Polymer Sci.* **1**, 581 (1946)).

Both parameters express the growth rate by means of addition of monomer of the same kind to an activated end relative to the addition of a monomer of the other kind. Defining furthermore the mole ratio  $A/B$  as  $z$ , eq 4 is transformed into

$$\frac{dA}{dB} = z \frac{(\sigma z + 1)}{(z + \mu)} \quad \text{or} \quad \frac{dA}{dA + dB} = \left[ 1 + \frac{1}{z} \frac{(z + \mu)}{(\sigma z + 1)} \right]^{-1} \quad (4a)$$

Figures 1, 2, and 3 show plots of eq 4a as a function of the mole fraction  $A/A+B$  in the monomer residue for a set of various values of the parameters  $\sigma$  and  $\mu$ . The straight line corresponds to a situation in which monomer composition and instantaneous polymer composition are

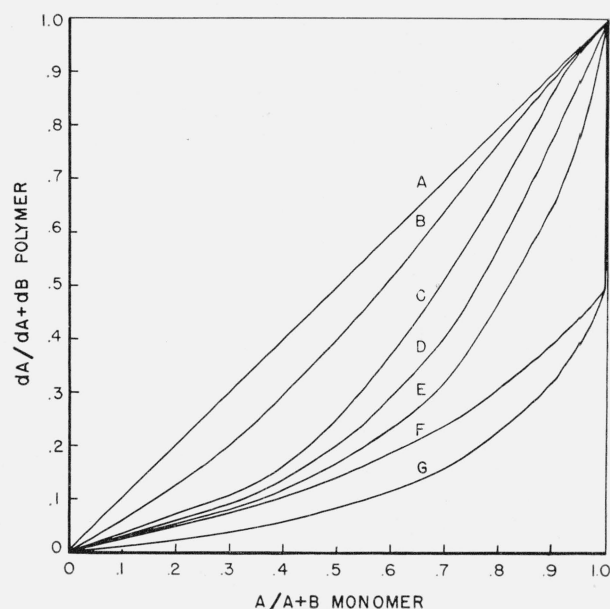


FIGURE 1. Plot of instantaneous mole fraction of component  $A$  in polymer as function of mole fraction of  $A$  in monomer mixture.

A,  $\mu=1, \sigma=1$ ; B,  $\mu=2, \sigma=1$ ; C,  $\mu=5, \sigma=1$ ; D,  $\mu=5, \sigma=1/2$ ; E,  $\mu=5, \sigma=1/3$ ; F,  $\mu=5, \sigma=0$ ; G,  $\mu=10, \sigma=0$ .

always equal. That is,  $\sigma$  and  $\mu$  must both equal unity. In some instances, (figs. 2 and 3) it will be noted that the curves intersect the diagonal, indicating that for a particular monomer charge the above-mentioned equality between the two compositions holds true. The meaning of this special case is discussed below. It is easy to visualize the limiting trends of these curves. For instance, large  $\mu$  and small  $\sigma$ , that is, preferential  $B$ - $B$  and  $A$ - $B$  addition must have the effect of



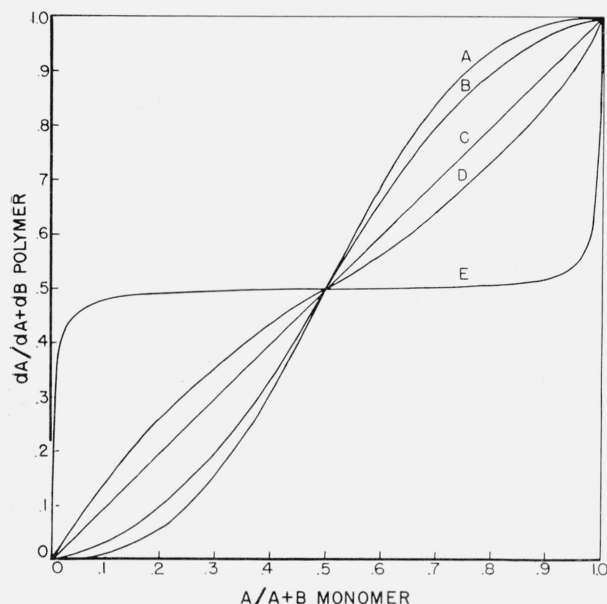


FIGURE 2. Plot of instantaneous mole fraction of component *A* in polymer as function of mole fraction of *A* in monomer mixture.

A,  $\mu=\sigma=100$ ; B,  $\mu=\sigma=5$ ; C,  $\mu=\sigma=1$ ; D,  $\mu=\sigma=0.5$ ; E,  $\mu=\sigma=0.01$ .

producing a copolymer deficient in *A* up to relatively high percentages of *A* in the monomer. The corresponding plots in figure 1 must therefore be of the type of *F* or *G*. If both  $\sigma$  and  $\mu$  are very small, the copolymer will be predominantly of the alternating type and  $dA/dA+dB$  will be close to 0.5 over a wide range of monomer composition, as shown in curve *E* of figure 2. Finally, if both  $\sigma$  and  $\mu$  are very large no copolymer is formed, except in a very narrow range around  $A/A+B=0.5$ , where there occurs a transition from pure polymer *B* to pure polymer *A*. Curve *A* in figure 2 illustrates the approach to this situation. In principle, it is possible to determine from graphs of this type the values of the constants  $\sigma$  and  $\mu$ , if the limiting slopes when *A* and *B*, respectively, approach zero are known. Substitution of  $A/A+B=z/z+1$  into eq 4a leads to the result

$$\lim d \left[ \frac{dA}{dA+dB} \right] / d \left[ \frac{A}{A+B} \right] = \begin{cases} \frac{1}{\mu}; & \text{when } \frac{A}{A+B} \rightarrow 0, \\ \frac{1}{\sigma}; & \text{when } \frac{A}{A+B} \rightarrow 1 \end{cases} \quad (4b)$$

Integration of eq 4a gives the number of moles of monomer *B* left at any instant of the reaction

as function of the composition *z* of the residue, namely,

$$\ln \frac{B_0}{B} = \frac{\mu}{\mu-1} \ln \frac{z}{z_0} + \frac{1-\sigma\mu}{(1-\sigma)(1-\mu)} \ln \frac{(\sigma-1)z - (\mu-1)}{(\sigma-1)z_0 - (\mu-1)} \quad (6)$$

where  $B_0$  and  $z_0$  are the initial values of *B* and *z*. This equation forms at present the basis for the determination of the parameters  $\sigma$  and  $\mu$  from an analysis of the copolymer composition. Applications will be discussed in the next section. First, however, we shall consider some general properties of the function represented by eq 6. Figure 4 shows a series of plots of  $\log B_0/B$  versus  $\log z/z_0$  for fixed values of  $z_0=0.4$  and  $\mu=5$ . If the rates of addition are independent of the nature of the active ends,  $\sigma=1/\mu$ , and a straight line is obtained. If active ends *A* increasingly favor the addition of monomer *B*, and ends *B* also favor the addition of *B*-type monomer ( $\mu=5$ ), the lines are still practically straight. The slopes become smaller due to the slower disappearance of monomer *A*, although the variations are small and hence determinations of  $\mu$  from such plots inaccurate.

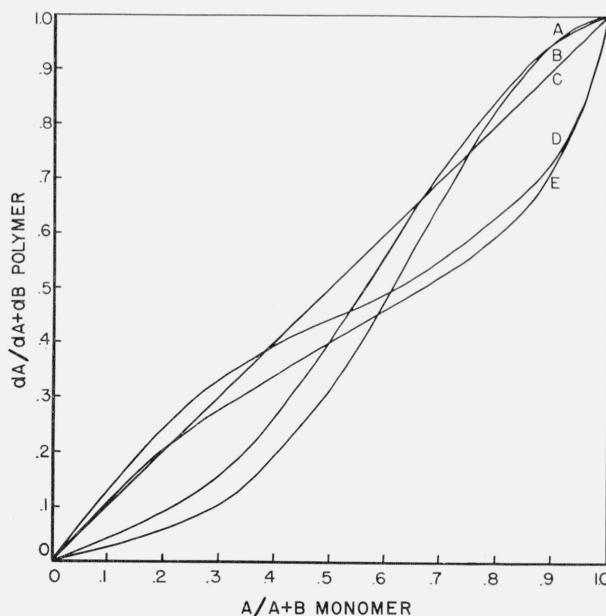


FIGURE 3. Plot of instantaneous mole fraction of component *A* in polymer as function of mole fraction of *A* in monomer mixture.

A,  $\mu=10$ ,  $\sigma=4$ ; B,  $\mu=5$ ,  $\sigma=3$ ; C,  $\mu=1$ ,  $\sigma=1$ ; D,  $\mu=0.5$ ,  $\sigma=0.2$ ; E,  $\mu=0.8$ ,  $\sigma=0.2$ .

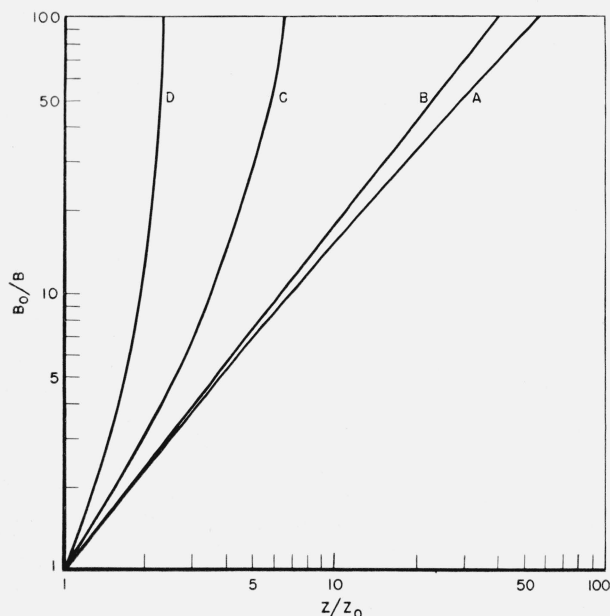


FIGURE 4. Plots of  $\log B_0/B$  vs  $\log z/z_0$ .

$z_0=0.4$ ;  $\sigma=5$ . A,  $\sigma=0$ ; B,  $\sigma=1/\mu$ ; C,  $\sigma=2$ ; D,  $\sigma=5$ .

The final polymer formed consists, in these examples, entirely of species A,  $z = \infty$ , for  $B=0$ . When  $\mu > 1$  and  $\sigma > 1$ , A-A and B-B linkages are more probable than cross-overs. The corresponding curves exhibit an upward curvature and possess a vertical asymptote shifting to the left as  $\sigma$  increases. In other words, the final polymer formed is a copolymer of fixed composition. Under such conditions the ratios between the rates balance the concentration ratios in the monomer residue in such a way that the polymer composition equals the composition of the monomer mixture or

$$\frac{dA}{dB} = \frac{A}{B}$$

Relation 4a then gives for the critical composition  $z_c$

$$z_c = \frac{\mu - 1}{\sigma - 1} \quad (7)$$

Thus  $\sigma$  and  $\mu$  must both be either smaller or larger than unity.

The fact that there exists a mixture of definite composition that copolymerizes without changing its composition, suggests an analogy with the familiar azeotropic mixtures often encountered in distillation processes [31]. One can construct curves analogous to distillation curves by considering the sum of the rates of consumption of

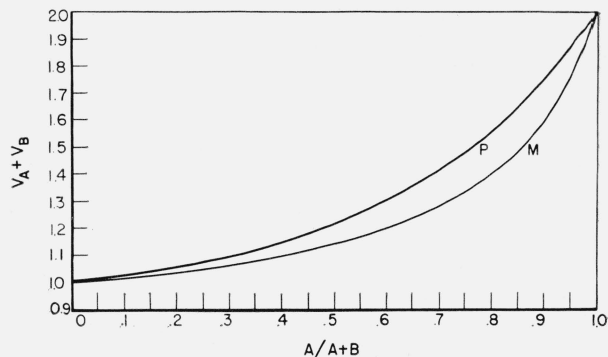


FIGURE 5. Plot of over-all rate for unit concentration of radical  $V_A + V_B$  on an arbitrary scale vs mole fraction of A in monomer (M) and in polymer (P).

$k_{gA}(A) = 2k_{gB}(B)$ ;  $\mu = 1.5$ ;  $\sigma = 0.5$ .

each monomer species as a function of the composition. Specifically, one may plot the over-all rate of polymerization  $V_A + V_B$  for unit concentration of free radicals [31]:

$$V_A + V_B = -\frac{1}{A+B} \frac{d}{dt} (A+B) \frac{1}{\sum n_{rs}(A) + \sum n_{rs}(B)}$$

By combining eq 2 and 3a the following result is obtained:

$$V_A + V_B = \frac{z(\sigma z + 1) + z + \mu}{z + 1} \frac{1}{\frac{\sigma z}{k_{gA}(A)} + \frac{\mu}{k_{gB}(B)}}$$

Figures 5 and 6 show such plots, assuming A-A addition to be twice as fast as B-B growth. The curves for the polymer (P) are constructed from eq

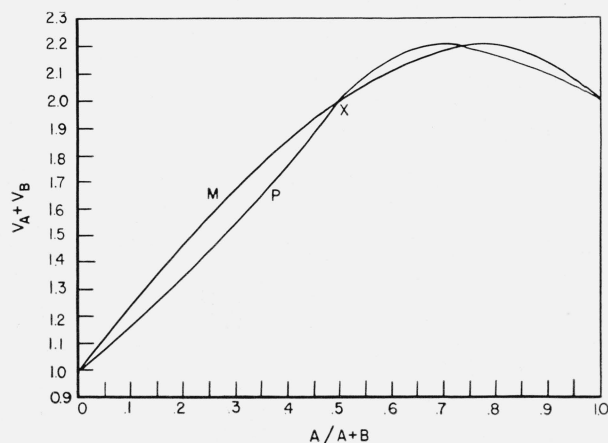


FIGURE 6. Plot of  $V_A + V_B$  on an arbitrary scale vs mole fraction of A in monomer (M) and in polymer (P), showing "azeotropic" composition X.

$k_{gA}(A) = 2k_{gB}(B)$ ;  $\mu = \sigma = 0.5$ .

4a. The curves for the monomer ( $M$ ) represent  $V_A + V_B$  as a function of  $A/A+B = z/z_0 + 1$ , according to the expression above. The abscissas of conjugate points on the two lines  $P$  and  $M$  indicate the composition of the copolymer and the composition of the corresponding monomer residue, respectively. Figure 6 depicts an "azeotrope." It will be noted that here the composition  $X$  does not correspond to an extremum in the curves, which represents a necessary thermodynamic condition for azeotropic boiling mixtures. Clearly the second intersection in figure 6 does not indicate a common composition for polymer and monomer. The discussion of these curves follows otherwise familiar lines. If  $\mu$  and  $\sigma$  are both smaller than unity, that is, if cross-combinations are preferred, one derives from eq 6 that  $z$  never reaches the critical value  $z_c$  but approaches zero or infinity, depending on whether  $z_0$  is respectively smaller or greater than  $z_c$ . If both reactivity ratios exceed unity, then the azeotropic composition is gradually approached.

It is of interest to follow the changes in composition taking place in the course of the copolymerization. Figure 7 depicts the relation between the instantaneous and total copolymer composition and the percentage conversion. Such curves are computed in the following manner. The extent of reaction, that is, the ratio between

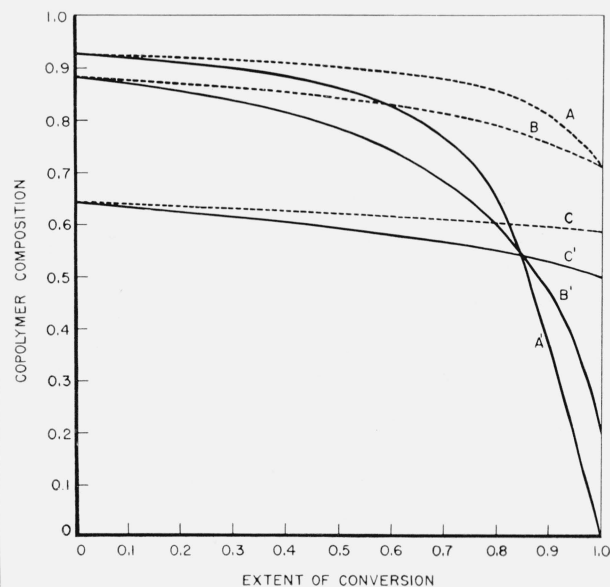


FIGURE 7. Instantaneous (full lines) and total composition (dashed lines) as function of the extent of conversion.

A, A',  $\mu=5$ ,  $\sigma=1/\mu$ ,  $z_0=0.4$ ; B, B',  $\mu=5$ ,  $\sigma=2$ ,  $z_0=0.4$ ; C, C',  $\mu=5$ ,  $\sigma=\mu$ ,  $z_0=0.7$ .

the weight of polymer at a given instant and the initial weight of the monomer mixture is given by the equation:

$$\frac{w_p}{w_0} = \frac{\left(1 - \frac{B}{B_0} \frac{z}{z_0}\right) M_1 z_0 + \left(1 - \frac{B}{B_0}\right) M_2}{M_1 z_0 + M_2} \quad (8)$$

$B/B_0$  and  $z/z_0$  have the same meaning as in eq 6.  $M_1$  and  $M_2$  are the molecular weights of the two monomers. With the aid of eq 6,  $B/B_0$  can be eliminated and  $w_p/w_0$  obtained as function of  $z/z_0$ . The instantaneous copolymer composition is directly given by eq 4a. The total composition resulting up to a given instant equals:

$$\int_0^{w_p} \frac{dB}{dA + dB} dw_p = \frac{1 - \frac{B}{B_0}}{(z_0 + 1) - \frac{B}{B_0}(z + 1)}, \quad (9)$$

and is again obtained with the aid of eq 6. As is obvious, the difference between instantaneous and total values increases with time and is more pronounced for systems with widely different reactivity ratios. In case an azeotrope exists, and the initial composition has been suitably chosen, the changes are slight as shown in curves  $C$  and  $C'$ . On the whole, the total copolymer composition does not change very much over a wide range of conversion. These variations can be eliminated by compensatory addition of the more active species during the course of the polymerization.

#### 4. Over-all rate of reaction

It is evident that the calculation of the average copolymer composition does not require a knowledge of the total concentration of free radicals but merely the ratio of  $A$ - and  $B$ -type radicals. For the over-all reaction rate, however, this information is required and obtained in the following manner. In a steady state and for the simplest case of a catalyzed reaction, we can write

$$\begin{aligned} \frac{d}{dt}(A^* + B^*) &= IC - k_t(A, A)A^{*2} - \\ &\quad 2k_t(A, B)A^*B^* - k_t(B, B)B^{*2} = 0, \end{aligned} \quad (3b)$$

where

$$A^* = \sum n_{rs}(A) \quad B^* = \sum n_{rs}(B)$$

Combination of eq 3a, 3b, and 2 then leads to the

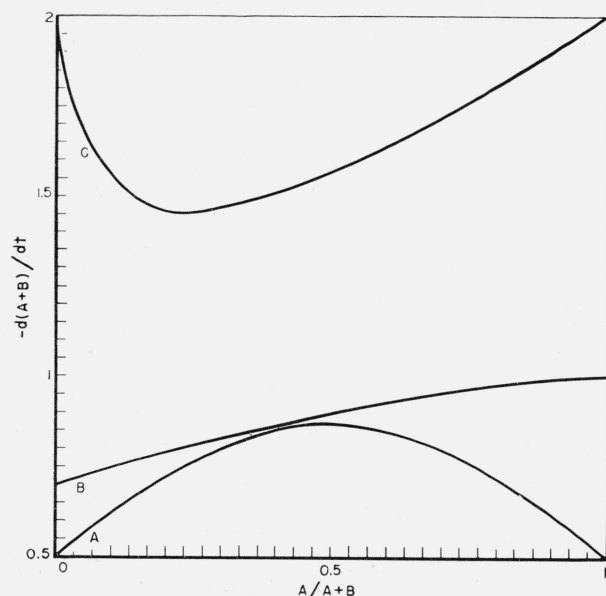


FIGURE 8. Plots of copolymerization rate on an arbitrary scale vs composition of monomer mixture according to eq 2a.

A,  $\beta=\gamma=1$ ,  $\mu=\sigma=0.5$ , scale multiplied by 4; B,  $\beta=\gamma=2$ ,  $\mu=\sigma=1$ ; C,  $\beta=1$ ,  $\gamma=1/6$ ,  $\mu=0.5$ ,  $\sigma=2$ .

following expression for the over-all rate of copolymerization [26]:

$$-\frac{d}{dt}(A+B) = \alpha \frac{\sigma A^2 + 2AB + \mu B^2}{(A^2 + \beta AB + \gamma B^2)^{1/2}} \quad (2a)$$

where:

$$\alpha = \left[ \frac{IC}{k_t(A,A)} \right]^{1/2} k_{gB}(A); \beta = \frac{2\mu}{\sigma} \frac{k_{gA}(A)}{k_{gB}(B)} \frac{k_t(A,B)}{k_t(A,A)};$$

$$\gamma = \frac{\mu^2}{\sigma^2} \left[ \frac{k_{gA}(A)}{k_{gB}(B)} \right]^2 \frac{k_t(B,B)}{k_t(A,A)} = \left( \frac{\beta}{2} \right)^2 \frac{k_t(A,A)k_t(B,B)}{k_t(A,B)^2}.$$

It should be noted again that in this derivation the initiation is described by a single constant  $I$ . This restricts the generality of this equation. For it is possible that the rate of production of the initial radicals varies with the composition of the mixture. In the most general case of the reaction scheme described, nine constants altogether would be needed to describe the process completely. As is to be expected under the assumptions made, the rate is proportional to the square root of the catalyst concentration, a familiar result in polymerization kinetics. Equation 2a contains besides  $\sigma$  and  $\mu$ , three constants. A knowledge of these allows a determination of the product

$$k_t(A,A)k_t(B,B)/k_t(A,B).$$

No use has as yet been made of these relations. Rate studies on the system styrene-methyl methacrylate have been presented by Norrish and Brookman [21]. However, they have been interpreted on the basis of an equation that assumes the concentrations  $A^*$  and  $B^*$  to be independent of the monomer ratio  $z$ . Plots of the rate (eq 2a) as function of the monomer composition  $A$  are shown in figure 8 for a few extreme cases.

## 5. Composition, Size, and Intramolecular Sequence Distributions

For the considerations hitherto presented, it is necessary only to know the total concentrations of radicals  $\Sigma n_{rs}(A)$  and  $\Sigma n_{rs}(B)$ , regardless of size and composition. In order to obtain the distribution of polymer sizes and compositions, we must consider the mode of production of individual radical chains of specified chain length and composition. From the postulated mechanism (eq 1), we find for the rate of production of these radicals:

$$\begin{aligned} \frac{dn_{rs}(A)}{dt} = & k_{gA}(A)An_{r-1,s}(A) + k_{gA}(B)An_{r-1,s}(B) - \\ & k_{gA}(A)An_{rs}(A) - k_{gB}(A)Bn_{rs}(A) - \\ & k_t(A,A)n_{rs}(A)\Sigma n_{ik}(A) - \\ & k_t(A,B)n_{rs}(A)\Sigma n_{ik}(B) \end{aligned} \quad (3c)$$

$$\begin{aligned} \frac{dn_{rs}(B)}{dt} = & k_{gB}(B)Bn_{r,s-1}(B) + k_{gB}(A)Bn_{r,s-1}(A) - \\ & k_{gB}(B)Bn_{rs}(B) - k_{gA}(B)An_{rs}(B) - \\ & k_t(B,B)n_{rs}(B)\Sigma n_{ik}(B) - \\ & k_t(A,B)n_{rs}(B)\Sigma n_{ik}(A). \end{aligned}$$

Equation 3c may be compared with the corresponding eq 3 for the total concentrations of A- and B-radicals and interpreted in the same manner. The positive terms refer to the growth of smaller chains to the desired size by monomer addition, and the negative ones measure the rate of disappearance of the radicals in question by either further growth or termination. Equation 3c holds for  $r$  and  $s$  both larger than unity. The rate of production of species  $n_{10}(A)$  and  $n_{01}(B)$  is governed by the rate of initiation such that in the first set of eq 3c the positive terms are replaced by  $I_A A$  and in the second one by  $I_B B$  or corresponding expressions involving the catalyst concentration. In a steady state the left-hand sides

of eq 3c vanish. The following quantities may be defined:

$$\begin{aligned}\omega(A) &= \frac{k_{gA}(A)A}{k_{gA}(A)A + k_{gB}(A)B + k_t(A,A)\Sigma n_{ik}(A) + k_t(A,B)\Sigma n_{ik}(B)} \\ \omega(B) &= \frac{k_{gB}(B)B}{k_{gB}(B)B + k_{gA}(B)A + k_t(B,B)\Sigma n_{ik}(B) + k_t(A,B)\Sigma n_{ik}(A)} \\ x &= \frac{k_{gB}(A)k_{gA}(B)}{k_{gA}(A)k_{gB}(B)} = \frac{1}{\sigma\mu}.\end{aligned}$$

It will be noted that  $\omega(A)$  represents the probability of formation of an  $A-A$  linkage by propagation,  $\omega(B)$  that of a  $B-B$  bond.  $x$  measures the probability of occurrence of  $B-A$  and  $A-B$  linkages relative to that of  $A-A$  and  $B-B$  bonds. The solution of eq 3c has been shown by Simha and Branson [26] to be

$$\begin{aligned}n_{rs}(A) &= \left[ \frac{I_A}{k_{gA}(A)} \sum_{j \geq 1} \binom{r-1}{j} \binom{s-1}{j-1} x^j + \right. \\ &\quad \left. \frac{I_B}{k_{gB}(A)} \sum_{j \geq 1} \binom{r-1}{j-1} \binom{s-1}{j-1} x^j \right] \omega(A)^r \omega(B)^s \\ n_{rs}(B) &= \left[ \frac{I_A}{k_{gA}(B)} \sum_{j \geq 1} \binom{r-1}{j-1} \binom{s-1}{j-1} x^j + \right. \\ &\quad \left. \frac{I_B}{k_{gB}(B)} \sum_{j \geq 1} \binom{r-1}{j-1} \binom{s-1}{j} x^j \right] \omega(A)^r \omega(B)^s. \quad (3d)\end{aligned}$$

Equation 3d may be interpreted in the following manner [26]: The terms multiplied by  $I_A$  give the total number of possibilities of producing a chain of specified composition by initiation through an  $A$ -radical. For each combinatory factor in the sum is a measure of the number of ways in which one possible internal arrangement characterized by a fixed number of  $A-A$ ,  $B-B$ ,  $A-B$  and  $B-A$  configurations may be realized by permutations. The exponential factors indicate the probability of occurrence of these configurations. The summation is then carried out over all possible internal arrangements compatible with the condition of having  $r$   $A$ -units and  $s$   $B$ -units. It is taken between the extremes of having one long sequence of  $A$ -units followed by one sequence of  $B$ -units, ( $j=1$ ), and the opposite extreme of a checker board arrangement of these two monomers. The  $I_B$  terms then stand for chains initiated by a  $B$ -radical. The meaning of the last equation may be seen also by specializing to the case  $\sigma\mu=1$ , in which propagation is independent of the nature of the growing end. Equation 3d then reduces to [10]

$$\begin{aligned}n_{rs} &= n_{rs}(A) + n_{rs}(B) = \left[ \frac{I_A}{k_{gA}(A)} \binom{r+s-1}{s} + \right. \\ &\quad \left. \frac{I_B}{k_{gB}(B)} \binom{r+s-1}{r} \right] \omega(A)^r \omega(B)^s. \quad (3e)\end{aligned}$$

Clearly the first term enumerates all ways of obtaining the polymer  $n_{rs}$  from a nucleus  $n_{10}$ ; the second term from a nucleus  $n_{01}$ .

From the known radical distribution, eq 3d, we obtain the distribution of stable polymer by means of the relations:

Combination:

$$\begin{aligned}\frac{dN_{rs}}{dt} &= k_t(A, A) \sum_{i, k} n_{r-i, s-k}(A) n_{ik}(A) + \\ &\quad 2k_t(A, B) \sum_{i, k} n_{r-i, s-k}(A) n_{ik}(B) + \\ &\quad k_t(B, B) \sum_{i, k} n_{r-i, s-k}(B) n_{ik}(B).\end{aligned}$$

Disproportionation:

$$\begin{aligned}\frac{dN_{rs}}{dt} &= n_{rs}(A) [k_t(A, A) \sum n_{ik}(A) + k_t(A, B) \sum n_{ik}(B)] + \\ &\quad n_{rs}(B) [k_t(B, B) \sum n_{ik}(B) + k_t(A, B) \sum n_{ik}(A)]\end{aligned} \quad (10)$$

Equation 10 determines the instantaneous distribution of sizes and compositions in a copolymer formed from a monomer mixture of a given composition  $A/A+B$ , which, in turn, determines the values of  $\omega(A)$  and  $\omega(B)$ . If the rate of the reaction has been measured, integration then yields the total distribution obtained up to a given instant or degree of conversion.

For the practically important case of long chains eq 3d has been simplified by Stockmayer [28] in a manner analogous to that for simple polymers [12]. It will be noted that for the latter case ( $s=0$ ), eq 3e reduces to

$$n_r = \frac{I}{k_g} \omega^r = \frac{I}{k_g} \left[ \frac{A}{A + \frac{k_t}{k_g} \Sigma n_i} \right]^r,$$

the result obtained by Herington and Robertson [12] for the distribution of radical lengths. Its physical significance is obvious. Since  $\omega$  deviates from unity only slightly because of the small concentration of radicals present,  $\omega^r$  can, in a good approximation, be replaced for large  $r$  by  $e^{-(1-\omega)r}$ .

The final result is best expressed in terms of the number average chain length  $\lambda$  of radicals, which equals the ratio between the rate of reaction and the rate of production (or destruction) of radicals. Inserting this value and noting that the total concentration of radicals is obtained from an equation analogous to eq 3b, one finds for the fraction of radicals of specified size [12]:

$$\frac{n_r}{\sum n_i} = \frac{1}{\lambda} e^{-\frac{r}{\lambda}}.$$

To obtain the corresponding expressions for copolymers we denote the total chain length  $r+s$  by  $l$ . Deviations in the composition of a chain from the average value as given by eq 4a will be measured by the quantity

$$y = \frac{r}{r+s} - \frac{dA}{dA+dB} = \frac{r}{l} - p_0. \quad (11)$$

As we are concerned with large values of  $l$ , the sums in eq 3d may be approximated by integrals and the individual terms expressed by means of Stirling's formula. Considering that the deviation from the average composition will not be very large in long chains, one can furthermore expand the relevant expressions in terms of  $y$ . The final result may be expressed as a function of  $l$  and  $y$  [28]

$$w(l, y) dl dy = \exp\left(-\frac{l}{\lambda}\right) \frac{l}{\lambda^2} dl \cdot \left[\frac{l}{2\pi p_0(1-p_0)\kappa}\right]^{\frac{1}{2}} \exp\left(-\frac{ly^2}{2p_0(1-p_0)\kappa}\right) dy, \quad (12)$$

which gives the weight fraction of radicals with polymerization degrees between  $l$  and  $l+dl$  and composition deviations between  $y$  and  $y+dy$ , irrespective of whether they terminate in  $A$ - or  $B$ -units.  $\kappa$  is defined by the relation

$$\kappa = [1 - 4p_0(1-p_0)(1-\sigma\mu)]^{\frac{1}{2}} = \frac{\sigma A^2 + 2\sigma\mu AB + \mu B^2}{\sigma A^2 + 2AB + \mu B^2}. \quad (13)$$

It is a measure of the spread of the composition distribution.  $\lambda$  is again the number average degree of polymerization of radicals

$$\lambda = -\frac{d}{dt} (A+B) \cdot [k_t(A,A)A^{*2} + 2k_t(A,B)A^*B^* + k_t(B,B)B^{*2}]^{-1}, \quad (14)$$

employing the notation of eq 3b and noting that the factor in the bracket represents the total rate of destruction of radicals which equals the rate of production in the steady state. The first factor, the over-all rate of the reaction can be expressed as in eq 2a or by corresponding expressions for other reaction mechanisms. It is assumed in eq 12 that monomers  $A$  and  $B$  have equal molecular weights.

The instantaneous size distribution of the stable polymer follows from eq 10. If termination occurs by disproportionation, the weight fraction of copolymer in the specified range of  $l$  and  $y$  is directly given by eq 12. If a fraction  $\rho$  of the radical chains is terminated by combination, the weight fraction is obtained by multiplying eq 12 by a factor

$$1 - \rho + \frac{\rho l}{2\lambda}.$$

Thus in the approximations used to simplify eq 3d and granted the validity of the reaction scheme 1 and of eq 4, the distribution function consists of two factors. One characterizes the distribution of molecular weights and the other the distribution of molecular composition for a fixed molecular weight. The specific nature of the termination process affects the former factor, but not the composition distribution.

Finally, one derives from eq 12 the chain-length distribution irrespective of composition by integration over all compositions,

$$w(l) dl = \int_0^\infty w(l, y) dy \cdot dl = e^{-\frac{l}{\lambda}} \frac{l}{\lambda^2} dl. \quad (12a)$$

Equation 12a has the same form as the result obtained for the instantaneous distribution in pure polymers produced by disproportionation [12]. The distribution of composition fluctuations is

$$w(y) dy = \int_0^\infty w(l, y) dl \cdot dy = \frac{3d\eta}{4(1+\eta^2)^{5/2}} \quad \text{with} \quad \eta = \left(\frac{\lambda}{2p_0(1-p_0)\kappa}\right)^{1/2} y. \quad (12b)$$

Plots of the expression (eq 12) as function of the reduced variables  $l/\lambda$  and  $\eta$  are shown in figures 9 and 10, respectively, as presented by Stockmayer [28]. It will be noted that large values of  $\eta$ , i. e., large deviations from the average composition, occur primarily in shorter chains, the longer chains



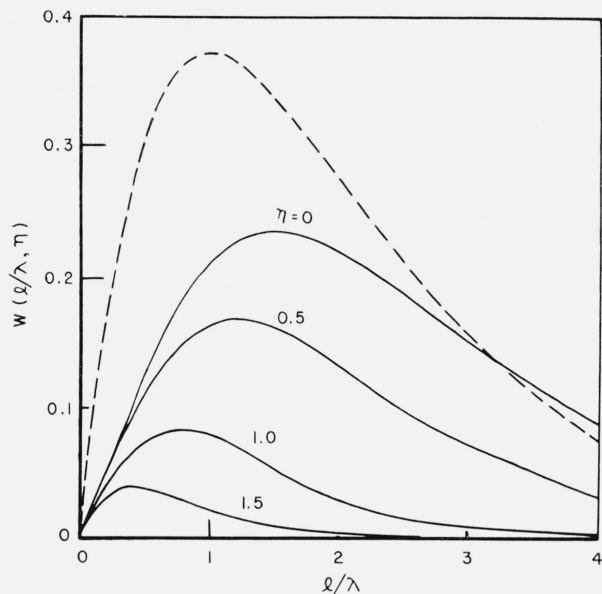


FIGURE 9. Full lines: Chain length distribution, eq 12, (weight fractions), as function of reduced chain length  $l/\lambda$  for fixed values of the reduced composition deviation  $\eta$ . Dotted line: Chain length distribution, eq 12a, irrespective of chain composition.

having mainly the average composition. Finally, the composition distribution (eq 12b) is shown in figure 11 for different values of the parameter  $\kappa$ . With increasing value of  $\kappa$ , that is, increasing values of  $\sigma/\mu$  for a fixed  $p_0$ , the fluctuations in composition become larger. This is understandable, since in this instance self addition of  $A$ - and  $B$ -units becomes increasingly preferred. However, it will be seen that the deviations from the mean value  $y=0$  are not large. Actually it can be derived from eq 12b that 88 percent by weight of the copolymer is found in the range  $|y| < [2p_0(1-p_0)\kappa/\lambda]^{1/2}$ , which is small for large values of  $\lambda$ . It should be noted again that application of these results to a complete copolymer product requires a knowledge of the complete reaction mechanism which determines the variation of the parameters  $\lambda$  and  $\kappa$  with average composition and conversion. No quantitative data seem to be available. Fractionation of various copolymer systems has actually indicated the existence of a dispersion in respect to composition [13, 17, 27].

The discussion of eq 3d has shown what is obvious, that even for a fixed composition in a given chain, there are a variety of possible internal arrangements of the species  $A$  and  $B$  in the chain corresponding to sequences of identical

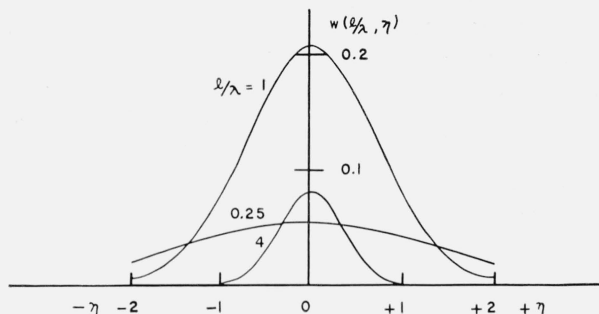


FIGURE 10. Composition distribution, eq 12, as function of the reduced composition deviation  $\eta$  for fixed values of the reduced chain length  $l/\lambda$ .

units of varying lengths. The frequency of occurrence of such sequences can be calculated and is of interest in connection with questions of structure [1,25,31] in copolymers. For sufficiently long chains the probabilities  $P_i(A)$  and  $P_i(B)$  of sequences of  $i$   $A$ - or  $B$ -units produced by propagation are given by

$$\left. \begin{aligned} P_i(A) &= [1 - \omega(B)][\omega(A)]^{i-1}[1 - \omega(A)] \\ P_i(B) &= [1 - \omega(A)][\omega(B)]^{i-1}[1 - \omega(B)] \\ P_0(A) &= \omega(B); P_0(B) = \omega(A) \end{aligned} \right\} \quad i \geq 1 \quad (15)$$

The  $\omega$ 's have the same meaning as in eq 3d, namely, that of propagation probabilities  $A$ - $A$  and  $B$ - $B$ . The validity of eq 15 is then immediately evident. Here the  $P_i$ 's are normalized so as to represent fractions of the total number of  $A$ - or  $B$ -sequences, respectively. If based on the average concentration of  $A$ ,  $P_i(A)$  is multiplied by  $dB/dA + dB$ .

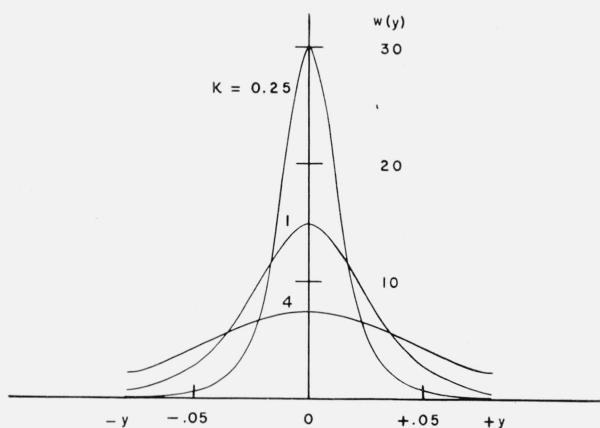


FIGURE 11. Composition distribution, eq 12b, as function of the composition deviation  $y$  from the mean for fixed values of  $\kappa$ , eq 13, and assuming  $\frac{\lambda}{2p_0(1-p_0)} = 400$ .

If termination is effected by combination, the distribution (eq 15) of sequences in the radical chains is not strictly identical with that in the stable copolymer. Neglecting the effect of termination altogether, we simplify the equation for  $\omega(A)$  and  $\omega(B)$  to:

$$\omega(A) = \frac{\sigma A}{\sigma A + B}; \quad \omega(B) = \frac{\mu B}{A + \mu B} \quad (16)$$

If the polymer in question has been obtained for instance, by copolymerizing mono and divinyl units, eq 15 gives the distribution of chain lengths between cross links and a number average chain

$$\frac{1}{1 - \omega(A)} = 1 + \sigma \frac{A}{B},$$

length for a copolymer prepared from a monomer mixture containing  $B$  moles of cross-linking agent.

## IV. Experimental Studies

### 1. Determination of Reactivity Ratios

The first thorough experimental investigation of copolymerization reactions has been made by Lewis, Mayo, and Hulse [15, 18], in which the parameters  $\sigma$  and  $\mu$  were found for several pairs of monomers. As eq 6 cannot be solved readily for  $\sigma$  and  $\mu$ , the following procedure was adopted: Equation 6 can be transformed into

$$\mu = \frac{\log \frac{B_0}{B} - \frac{1}{p} \log \frac{1 - pz}{1 - pz_0}}{\log \frac{z_0}{z} + \log \frac{B_0}{B} + \log \frac{1 - pz}{1 - pz_0}}, \quad (6a)$$

where

$$p = (1 - \sigma)/(1 - \mu).$$

One experimental run gives a set of  $z, z_0$  and  $B, B_0$  values. Arbitrary values of  $p$  are then chosen, and the corresponding  $\mu$  is computed using eq 6a. The value for  $\sigma$  is obtained from the expression for  $p$ . A plot of  $\sigma$  versus  $\mu$  gives practically a straight line. A second run is utilized to get another  $\sigma$ - $\mu$  line. The intersection of two or more such curves then gives the unique values for  $\sigma$  and  $\mu$ , satisfying theoretically all runs. In practice the intersection of three lines form a triangle, the area of which is a measure of the experimental errors. On this basis [18] table 1 and figure 12 represent, as an example, the best data obtained by Mayo and Lewis on the copolymerization of

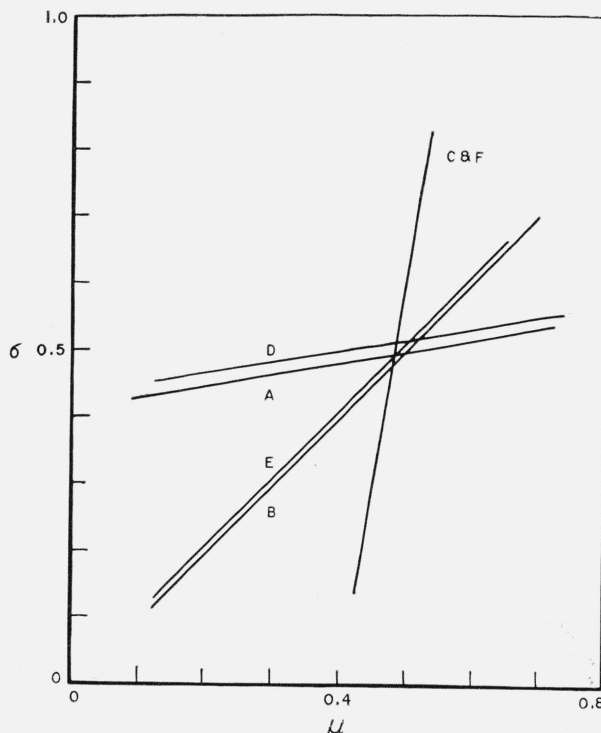


FIGURE 12. Determination of  $\mu$  and  $\sigma$  values from data in table 1.

styrene and methyl methacrylate. The difficulties involved in the analysis of a partially polymerized system have been emphasized [14]. Separation of monomers from the polymer has been in most cases open to improvement. The usual techniques have been the precipitation of the polymer by suitable combinations of solvents and vacuum distillation. In general these methods do not adequately separate the polymers, as shown by the fact that the results obtained by the above workers [18] differed considerably, depending on the procedure used for the isolation of the polymer. The technique finally developed utilizes the relatively high vapor pressure of frozen benzene at temperatures near  $0^\circ \text{C}$ . This method, known as the frozen benzene technique, involves several precipitations, after which the polymer is dissolved in benzene and then the solution quickly frozen. Subsequently the benzene is sublimed off under vacuum. The polymer is then in the form of a very fine powder, which is easily handled. By using such means for the isolation of polymer, results [15] were produced that are very accurate for work of this nature.

Almost all of the monomer pairs so far studied

TABLE 1. *Styrene-methyl methacrylate copolymerization*

Experiment	Concentration of unreacted monomer				Reaction time	Polymer			$\sigma$	$\mu$
	Original		Final							
	$A_0$	$B_0$	$A$	$B$						
$A$ -----	0.7980	0.2020	0.7435	0.1813	$hr$ 5	$wt\%$ 7.57	$Carbon\%$ 83.66	$Carbon\%$ {83.77 83.94	0.48 to 0.50	0.48 to 0.50
$B$ -----	.5010	.4990	.4571	.4556	5	8.74	76.52	76.61		
$C$ -----	.2021	.7979	.1828	.7468	2.68	7.05	69.13	69.11		
$D$ -----	.8064	.1996	.7450	.1796	89	7.53	83.98	84.00	0.48 to 0.52	0.48 to 0.52
$E$ -----	.5020	.4980	.4552	.4520	89	9.28	76.70	76.53		
$F$ -----	.1980	.8020	.1623	.7058	68.5	13.23	68.90	69.07		

have been those in which one monomer contained a different and easily analyzed element or group. In view of the availability and the high development of spectrometric and other physical methods of analysis [9, 16, 19], there is room for techniques using these methods for the study of copolymerization. Instead of analyzing the polymer, it should be possible to determine directly the composition of the monomer residue. One could place a sample of a polymerizing mixture in a high vacuum system and remove monomers from polymer by pumping off volatiles into a large residual volume or condensing in a liquid air trap. Then the volatiles could be analyzed by either mass, infrared, or ultraviolet spectrometry, depending on the nature of the system. An analysis of a relatively large bulk of residual monomers should be less subject to errors due to small amounts of monomers trapped in the polymer than an analysis of the polymer itself at low conversion. Such procedures should be particularly useful in copolymerization studies of isomers or compounds having small differences in their elemental analyses.

## 2. Summary of Reactivity Ratios

Table 2 summarizes the published results on monomer reactivities found by copolymerizing various pairs of monomers.<sup>5</sup> It is seen, for instance, that in the reaction of styrene and methyl methacrylate, the addition of styrene monomer to styrene radical occurs half as fast as the addition of methyl methacrylate monomer to styrene radical. Also methyl methacrylate monomer adds half as fast to a methyl methacrylate

radical as does styrene monomer. Furthermore, styrene monomer adds to styrene radical twice as fast as vinylidene chloride monomer to styrene radical. On the other hand, vinylidene chloride monomer adds to vinylidene chloride radical approximately one seventh as fast as styrene monomer. The estimated degrees of precision are indicated whenever given by the authors. In the case of references [3, 5, 7, 38, 39], the reactivity ratios were obtained from plots according to eq 4a by fitting the "best" curve. As an example, the system styrene-dichlorostyrene investigated by Alfrey, Merz, and Mark [5] is shown in figure 13.

A special case investigated is that wherein one of the monomers does not polymerize with itself

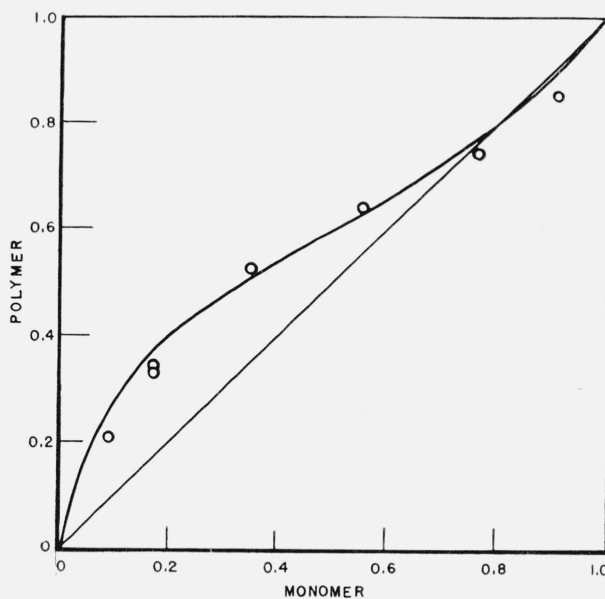


FIGURE 13. Plot of instantaneous concentration of dichlorostyrene in polymer vs concentration of dichlorostyrene in monomer according to eq 4a and data in [5].

<sup>5</sup> We are indebted to K. R. Henery-Logan and R. V. V. Nicholls for placing their results at our disposal prior to publication. The work was sponsored by the Office of Rubber Reserve.

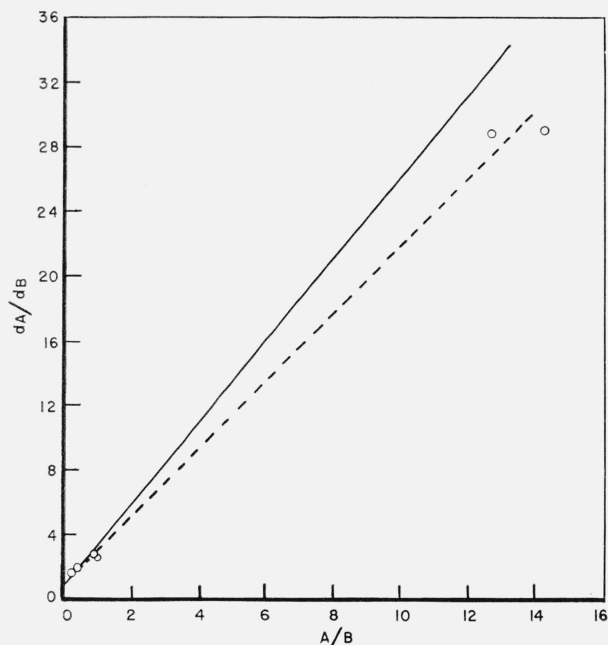


FIGURE 14. Plot of instantaneous mole ratio in polymer vs mole ratio in monomer for system styrene-diethyl chloromaleate according to data in [5].

but readily enters into copolymerization. Maleic anhydride [29] and its derivatives form a class of compounds exhibiting such a selectivity. Setting  $\mu=0$  in the first eq 4a results in a linear relation. An experimental test on the system styrene-diethyl chloromaleate is shown in figure 14. The full line  $\sigma=2.5$  is taken as the "best" value from a consideration of the data when plotted on a mole fraction basis.

The foregoing results substantiate rather well

the assumptions under which the composition eq 4 has been derived, at least for the relatively low degrees of conversion at which it may be expected to hold. In attempts to consider the effect of composition on the addition rates<sup>6</sup> equations have been derived [20] for the case that the rates depend not only on the nature of the radical ends, but also on the preceding unit in the chain. The effects are small, and their detection would require considerable experimental accuracy.

Extensions of eq 4 to three-component systems and generalization to  $n$ -components [34] have been presented. Analysis of one four-component and seven three-component systems formed from styrene, methyl methacrylate, acrylonitrile, and vinylidene chloride indicates agreement with theory within experimental error. It is assumed in this comparison that the reactivity ratios of a pair  $A-B$  are independent of the medium and equal to the ratios obtained in the copolymerization of  $A$  and  $B$  alone.

Most of the published and analyzed results refer to bulk systems. In order to make valid comparisons for the monomer pairs studied, we shall confine the further discussion to the data in table 2. Some investigations in emulsion systems have been undertaken. For instance, the pairs given under footnote 5 and also the styrene-acrylonitrile combination [15] have been analyzed both in bulk and in emulsion. In the main no significant differences between the  $\sigma-\mu$  values under the two different conditions are found.

<sup>6</sup> See also the discussion on page 524.

TABLE 2. Reactivity ratios  $\sigma$  and  $\mu$  for various monomer pairs

Monomer A	$\sigma$	Monomer B	$\mu$	Conditions	Reference
Styrene.....	0.520 $\pm$ .026	Methyl methacrylate.....	0.460 $\pm$ 0.026	60° C, 0.1 mole % benzoyl peroxide, bulk....	[42]
Do.....	.75	Methyl acrylate.....	.20	70° C, 0.4 mole % benzoyl peroxide, 40% monomer in toluene.	[5]
Do.....	.75 $\pm$ .07	do.....	.18 $\pm$ .02	60° C, 0.1 mole % benzoyl peroxide, bulk....	[42]
Do.....	.30 $\pm$ .10	Methacrylonitrile.....	.16 $\pm$ .06	do.....	[43]
Do.....	.29 $\pm$ .04	Methyl vinyl ketone.....	.35 $\pm$ .02	do.....	[43]
Do.....	.41 $\pm$ .08	Acrylonitrile.....	.04	do.....	[15]
Do.....	31	Allyl chloride.....	.032	70° C, 0.5 mole % benzoyl peroxide, bulk....	[3]
Do.....	0.54 $\pm$ .01	<i>p</i> -Chloroethyl acrylate.....	.10 $\pm$ .01	60° C, 0.1 mole % benzoyl peroxide, bulk....	[43]
Do.....	1.85 $\pm$ .05	Vinylidene chloride.....	.085 $\pm$ .010	do.....	[40]
Do.....	2.00 $\pm$ .10	do.....	.14 $\pm$ .05	do.....	[15]
Do.....	.55 $\pm$ .10	Vinyl acetate.....	.01 $\pm$ .01	do.....	[44]
Do.....	17 $\pm$ 3	Vinyl chloride.....	.02	do.....	[40]
Do.....	90 $\pm$ 20	Vinyl ethyl ether.....	0	do.....	[43]
Do.....	0.35 $\pm$ .025	Vinylthiophene.....	3.10 $\pm$ .45	60° C, 0.5 mole % benzoyl peroxide, bulk....	[44]
Do.....	.55 $\pm$ .025	$\alpha$ -Vinylpyridene.....	1.135 $\pm$ .08	do.....	[44]
Do.....	.23 $\pm$ .07	Butadiene.....	1.48 $\pm$ .08	50° C, 0.1 mole % benzoyl peroxide, bulk....	Footnote 5
Do.....	.78 $\pm$ .01	do.....	1.39 $\pm$ .03	60° C, 0.1 mole % benzoyl peroxide, bulk....	[43]
Do.....	1.38 $\pm$ .54	Isoprene.....	2.05 $\pm$ .45	50° C, 0.1 mole % benzoyl peroxide, bulk....	Footnote 5
Do.....	0.0	Chloroprene.....	6.30 $\pm$ .10	do.....	Do.

TABLE 2. Reactivity ratios  $\sigma$  and  $\mu$  for various monomer pairs—Continued

Monomer A	$\sigma$	Monomer B	$\mu$	Conditions	Reference
Styrene	.043 $\pm$ .09	Maleic anhydride	0	80° C, benzoyl peroxide, benzene solvent	[4]
Do	2.5	Diethyl chloromaleate	0	70° C, 0.4 mole % benzoyl peroxide, bulk	[3]
Do	0.13 $\pm$ .01	Monoethyl maleate	.035 $\pm$ .01	60° C, 0.2 mole % benzoyl peroxide, bulk	[41]
Do	8.5 $\pm$ .20	Dimethyl maleate	.03 $\pm$ .01	do	[41]
Do	5.0	Diethyl maleate	0	70° C, 0.4 mole % benzoyl peroxide, bulk	[5]
Do	6.52 $\pm$ .50	do	.005 $\pm$ .01	60° C, 0.1 mole % benzoyl peroxide, bulk	[42]
Do	0.19 $\pm$ .01	Maleonitrile	0	60° C, 0.2 mole % benzoyl peroxide, bulk	[41]
Do	.18 $\pm$ .10	Monoethyl fumarate	0.25 $\pm$ 0.10	do	[41]
Do	.21 $\pm$ .02	Dimethyl fumarate	.25 $\pm$ .015	do	[41]
Do	.30 $\pm$ .02	Diethyl fumarate	.070 $\pm$ .007	60° C, 0.1 mole % benzoyl peroxide, bulk	[42]
Do	.19 $\pm$ .03	Fumaronitrile	0	60° C, 0.2 mole % benzoyl peroxide, bulk	[41]
Do	16 $\pm$ 2	Trichloroethylene	.01 $\pm$ .01	60° C, 0.1 mole % benzoyl peroxide, bulk	[40]
Do	185 $\pm$ 20	Tetrachloroethylene	0	do	[40]
Do	37 $\pm$ 3	trans-Dichloroethylene	0	60° C, 0.2 mole % benzoyl peroxide, bulk	[41]
Do	210 $\pm$ 15	cis-Dichloroethylene	0	do	[41]
Do	10	trans-Dichloroethylene	0	68° C, 0.1 weight % benzoyl peroxide, bulk	[39]
Do	50-100	cis-Dichloroethylene	0	do	[39]
Do	1.16 $\pm$ .09	p-Methoxystyrene	0.82 $\pm$ .07	60° C, 0.1 mole % benzoyl peroxide, bulk	[35]
Do	1.015 $\pm$ .06	p-Dimethylamino-styrene	.84 $\pm$ .05	do	[35]
Do	0.74 $\pm$ .03	p-Chlorostyrene	1.025 $\pm$ .05	do	[35]
Do	.695 $\pm$ .02	p-Bromostyrene	0.99 $\pm$ .07	do	[35]
Do	.62 $\pm$ .05	p-Iodostyrene	1.25 $\pm$ .30	do	[35]
Do	.64 $\pm$ .05	m-Chlorostyrene	1.09 $\pm$ .23	do	[35]
Do	.55 $\pm$ .03	m-Bromostyrene	1.05 $\pm$ .21	do	[35]
Do	.28 $\pm$ .025	p-Cyanostyrene	1.16 $\pm$ .13	do	[35]
Do	.19 $\pm$ .02	p-Nitrostyrene	1.15 $\pm$ .20	do	[35]
Do	.20	2,5 Dichlorostyrene	0.80	70° C, 0.4 mole % benzoyl peroxide, bulk	[3]
Do	.56 $\pm$ .03	o-Chlorostyrene	1.64 $\pm$ .07	60° C, 0.5 mole % benzoyl peroxide, bulk	[46]
Methyl methacrylate	.67 $\pm$ .10	Methacrylonitrile	0.65 $\pm$ .06	60° C, 0.1 mole % benzoyl peroxide, bulk	[43]
Do	1.2 $\pm$ .14	Acrylonitrile	0.15 $\pm$ .07	60° C, 0.1 mole % benzoyl peroxide, bulk	[15]
Do	2.53 $\pm$ .1	Vinylidene chloride	.24 $\pm$ .03	do	[15]
Do	20 $\pm$ 3	Vinyl acetate	.015 $\pm$ .015	do	[44]
Do	10	Vinyl chloride	.1	68° C, 0.2-0.4 weight % benzoyl peroxide bulk	[38]
Do	0.395 $\pm$ .025	$\alpha$ -Vinyl pyridine	0.86 $\pm$ .06	60° C, 0.5 mole % benzoyl peroxide, bulk	[46]
Do	.25 $\pm$ .03	Butadiene	.75 $\pm$ .05	60° C, 0.1 mole % benzoyl peroxide, bulk	[43]
Do	.29 $\pm$ .03	p-Methoxystyrene	.32 $\pm$ .05	do	[35]
Do	.205 $\pm$ .02	p-Dimethylaminostyrene	.11 $\pm$ .02	do	[35]
Do	.405 $\pm$ .025	p-Methylstyrene	.44 $\pm$ .02	do	[35]
Do	.53 $\pm$ .025	m-Methylstyrene	.49 $\pm$ .02	do	[35]
Do	.415 $\pm$ .02	p-Chlorostyrene	.89 $\pm$ .05	do	[35]
Do	.395 $\pm$ .02	p-Bromostyrene	1.10 $\pm$ .25	do	[35]
Do	.36 $\pm$ .03	p-Iodostyrene	0.95 $\pm$ .20	do	[35]
Do	.47 $\pm$ .075	m-Chlorostyrene	.91 $\pm$ .11	do	[35]
Do	.48 $\pm$ .02	m-Bromostyrene	1.17 $\pm$ .25	do	[35]
Do	.22 $\pm$ .02	p-Cyanostyrene	1.41 $\pm$ .13	do	[35]
Do	.50 $\pm$ .03	o-Chlorostyrene	1.37 $\pm$ .10	60° C, 0.5 mole % benzoyl peroxide, bulk	[46]
Do	.50 $\pm$ .03	$\alpha$ -Methyl styrene	0.14 $\pm$ .01	do	[46]
Do	.41	2,5 Dichlorostyrene	2.55	68° C, 0.2-0.4 weight % benzoyl peroxide, bulk	[38]
Vinyl acetate	0.1 $\pm$ .1	Methyl acrylate	9 $\pm$ 2.5	60° C, 0.1 mole % benzoyl peroxide, bulk	[44]
Do	.7	Allyl chloride	0.67	68° C, 0.2-0.4 weight % benzoyl peroxide, bulk	[38]
Do	.60 $\pm$ .15	Allyl acetate	.45 $\pm$ .15	60° C, 0.1 mole % benzoyl peroxide, bulk	[43]
Do	.1	Vinylidene chloride	6	68° C, 0.2-0.4 weight % benzoyl peroxide, bulk	[38]
Do	.0 $\pm$ .03	do	3.6 $\pm$ .5	60° C, 0.1 mole % benzoyl peroxide, bulk	[40]
Do	.3	Vinyl chloride	2.1	68° C, 0.2-0.4 weight % benzoyl peroxide, bulk	[38]
Do	.35	Vinyl bromide	4.5 $\pm$ 1.2	60° C, 0.1 mole % benzoyl peroxide, bulk	[44]
Do	3.0 $\pm$ .1	Vinyl ethyl ether	0	do	[44]
Do	.23 $\pm$ .02	Vinyl chloride	1.68 $\pm$ .08	60° C, 0.1 mole % benzoyl peroxide, bulk	[44]
Do	0.17 $\pm$ .01	Diethyl maleate	.043 $\pm$ .005	60° C, 0.2 mole % benzoyl peroxide, bulk	[41]
Do	.011 $\pm$ .001	Diethyl fumarate	.444 $\pm$ .003	do	[41]
Do	.67	Trichloroethylene	0	68° C, 0.1 weight % benzoyl peroxide, bulk	[39]
Do	.66 $\pm$ .04	do	.01 $\pm$ .01	60° C, 0.5 mole % benzoyl peroxide, bulk	[44]
Do	5	Tetrachloroethylene	0	68° C, 0.2-0.4 weight % benzoyl peroxide, bulk	[38]
Do	6.8 $\pm$ .5	do	0	60° C, 0.1 mole % benzoyl peroxide, bulk	[40]
Do	0.85	trans-Dichloroethylene	0	68° C, 0.1 weight % benzoyl peroxide, bulk	[39]
Do	2.8	cis-Dichloroethylene	0	do	[39]

TABLE 2. Reactivity ratios  $\sigma$  and  $\mu$  for various monomer pairs—Continued

Monomer A	$\sigma$	Monomer B	$\mu$	Conditions	Reference
Vinyl Acetate.....	0.99±0.02	<i>trans</i> -Dichloroethylene.....	0.086±0.01	60° C, 0.2 mole % benzoyl peroxide, bulk.....	[41]
Do.....	6.3 ± .2	<i>cis</i> -Dichloroethylene.....	.018±.003	do.....	[41]
Acrylonitrile.....	.61±.04	Methyl vinyl ketone.....	1.78 ± .22	60° C, 0.1 mole % benzoyl peroxide, bulk.....	[43]
Do.....	.91±.1	Vinylidene chloride.....	0.37 ± .1	do.....	[15]
Do.....	4.05±.3	Vinyl acetate.....	.061±.013	60° C, 0.1 mole % benzoyl peroxide, 45 mole % monomer in acetonitrile.....	[44]
Do.....	3.28±.06	Vinyl chloride.....	.02 ± .02	60° C, 0.1 mole % benzoyl peroxide, bulk.....	[43]
Do.....	0.0 ± .04	Butadiene.....	.35 ± .08	50° C, 0.1 mole % benzoyl peroxide, bulk.....	Footnote 5.
Do.....	.03±.03	Isoprene.....	.45 ± .05	do.....	Do.
Do.....	.01±.01	Chloroprene.....	6.07 ± .53	do.....	Do.
Do.....	470	Tetrachloroethylene.....	0	60° C, 0.1 mole % benzoyl peroxide, bulk.....	[40]
Vinyl chloride.....	0.14	Vinylidene chloride.....	Large	68° C, 0.2-0.4 weight % benzoyl peroxide, bulk.....	[38]
Do.....	.77	Diethyl maleate.....	.009±.003	60° C, 0.2 mole % benzoyl peroxide, bulk.....	[41]
Do.....	.42	Dioctyl maleate.....	0	68° C, 0.2-0.4 weight % benzoyl peroxide, bulk.....	[38]
Do.....	.12±.01	Diethyl fumarate.....	.47 ± .05	60° C, 0.2 mole % benzoyl peroxide, bulk.....	[41]
Do.....	5.0	Pentene 1.....	.2	68° C, 0.2-0.4 weight % benzoyl peroxide, bulk.....	[38]
Do.....	2.05±.3	Isobutylene.....	.08 ± .10	60° C, 0.1 mole % benzoyl peroxide, bulk.....	[43]
Vinylidene chloride.....	0.35	Ethyl methacrylate.....	2.2	68° C, 0.2-0.4 weight % benzoyl peroxide, bulk.....	[38]
Do.....	.35	Butyl methacrylate.....	2.2	do.....	[38]
Do.....	12.2 ±2.0	Diethyl fumarate.....	0.046±.015	60° C, 0.1 mole % benzoyl peroxide, bulk.....	[40]
Do.....	3.8	Allyl chloride.....	.26	68° C, 0.2-0.4 weight % benzoyl peroxide, bulk.....	[38]
Maleic Anhydride.....	.03±.03	Stilbene.....	.03 ± .03	60° C, 0.1 mole % benzoyl peroxide, bulk.....	[41]
Do.....	.13 up	Allyl acetate.....	.0075 up	30° and 38.5° C, approximately 0.5 mole %.....	[7]
$\beta$ Chloroethyl acrylate.....	5.5 ±1	do.....	0	60° C, 0.1 mole % benzoyl peroxide, bulk.....	[43]
Do.....	4 ±1	Methallyl acetate.....	0	do.....	[43]
Do.....	0.9 ± .1	Methyl acrylate.....	.9 ± .1	do.....	[43]
<i>p</i> -Chlorostyrene.....	1.15±.05	<i>p</i> -Methylstyrene.....	.61 ± .03	do.....	[35]
Do.....	0.86±.08	<i>p</i> -Methoxystyrene.....	.58 ± .03	do.....	[35]
Do.....	.70±.08	<i>p</i> -Nitrostyrene.....	.91 ± .37	do.....	[35]
Chloroprene.....	3.41±.07	Butadiene.....	.059±.015	50° C, 0.1 mole % benzoyl peroxide, bulk.....	Footnote 5.
Do.....	3.65±.11	Isoprene.....	.133±.025	do.....	Do.

## V. Discussion

### 1. Remarks on Effect of Substituents in Organic Reactions

Tables 3 and 4 summarize the experimental information in a slightly different way by giving the relative reactivities of a series of different monomers vs a given radical, e. g., styrene. The scale is arbitrarily fixed by setting the reactivity of a monomer toward a radical of its own kind equal to unity. Values above unity then signify a higher activity than that exhibited by the radical in question toward the identical monomer, whereas values below unity signify a lower activity. Some of the values may be affected by large errors, as can be judged by the limits given for the  $\sigma$  and  $\mu$  values from which they were calculated.

The interpretation of these results in terms of the electronic structure and internal geometry of radical and monomer is no easy task. However, certain qualitative attacks, at least, can be made

TABLE 3. Relative reactivities of monomers with styrene radical shown in comparison with Hammett's  $\sigma$ -values for the aromatics

Monomer	Reactivity	Hammett's $\sigma$
Vinyl acetate.....	0.02	-----
Allyl chloride.....	.032	-----
Diethyl maleate.....	.2	-----
Diethyl chloromaleate.....	.4	-----
Vinylidene chloride.....	.5	-----
Isoprene.....	.73	-----
<i>p</i> -Methoxystyrene.....	.86	-0.268
<i>p</i> -Dimethylaminostyrene.....	.98	-.205
Styrene.....	1.00	.000
Methyl acrylate.....	1.33	-----
<i>p</i> -Chlorostyrene.....	1.35	+.227
<i>p</i> -Bromostyrene.....	1.44	.232
<i>m</i> -Chlorostyrene.....	1.56	.373
<i>p</i> -Iodostyrene.....	1.61	.276
<i>m</i> -Bromostyrene.....	1.82	.391
Methyl methacrylate.....	2.00	-----
Acrylonitrile.....	2.50	-----
<i>p</i> -Cyanostyrene.....	3.57	1.000
Butadiene.....	4.45	-----
Dichlorostyrene.....	5.00	-----
<i>p</i> -Nitrostyrene.....	5.26	1.27
Maleic anhydride.....	24.0	-----
Chloroprene.....	$\infty$	-----



along the lines established in the study of organic reactions of small molecules. That we are dealing here with large radicals is no objection, since we have established within the limits of the system studied, that the growth rates are independent of molecular size.

TABLE 4. *Relative reactivities of various monomers with various radicals*

Monomer	Radical type						
	Styrene	Methyl methacrylate	Acrylonitrile	Vinylidene chloride	Isoprene	Butadiene	Chloroprene
Styrene.....	1.0	2.0	25	7	0.5	0.7	0.2
Methyl methacrylate.....	2.0	1.0	7	4.1	---	1.3	---
Acrylonitrile.....	2.5	0.8	1.0	2.7	2.2	3.1	.2
Vinylidene chloride.....	0.5	.4	1.1	1.0	---	---	---
Isoprene.....	.7	---	33.0	---	1.0	---	.3
Butadiene.....	4.5	4.0	8	---	---	1.0	.3
Chloroprene.....	8	---	200	---	7.5	17.0	1.0

It is perhaps worthwhile to precede the discussion of the subject proper with a cursory and necessarily simplified summary of certain results and concepts regarding organic reactions. We need to consider the influence certain substituent groups such as  $\text{CH}_3$ ,  $\text{Cl}$ ,  $\text{NO}_2$ , etc., in vinyl-type monomers exert on the electronic configuration in the adjacent double bond. The presence of such groups in a benzene ring leads to a change, as compared with benzene, in the rates of further substitution and affects also the locus of substitution. These facts have been known for some time in classical organic chemistry.<sup>7</sup> They are caused by the tendency of an electrophilic group to attack the ring at the region of highest (relative) electron density. Furthermore, if the over-all density is reduced compared to that in benzene, the rate of reaction is accordingly reduced.

In considering the mechanisms of such distortions of the charge distribution, we shall somewhat arbitrarily separate two factors, inductive effects in the sense of Ingold<sup>8</sup> and resonance effects. The former lead to an increase or decrease of the over-all availability of electrons in the ring, the substituent acting as an electron source or sink. For instance, a methyl group

increases the electronic density in the ring and thus should increase the rate of substitution by an electrophilic agent while a chlorine atom, with its strong electron affinity, has the opposite tendency. Similarly, substituents such as  $\text{NO}_2$ ,  $\text{CN}$ , or  $\text{COOR}$  tend to diminish the electron density. Analogous effects by such groups are observed in addition reactions to double bonds in simple olefins. Resonance effects can determine the locus of attack. For instance, groups with an unshared pair of electrons such as  $\text{Cl}$ ,  $\text{OH}$ ,  $\text{NH}_2$ ,  $\text{C}_6\text{H}_5$ , contribute structures to the activated complex of the substitution reaction (see footnote 7) which make the ortho- and para-positions more negative



while no structure making the meta-position negative can be written. The resonance effect of  $\text{NO}_2$ ,  $\text{CN}$ ,  $\text{COOR}$ , and similar groups tends to leave the meta-position relatively more negative. Hence they are meta-directing. These directive effects persist in addition reactions to olefins. In general, ortho-para-directing substituents cause addition to proceed in accordance with Markownikoff's rule, meta-directing ones in opposition to it. These directive effects have also been explained without introducing explicitly the notion of resonance [23].

A quantitative measure of changes in electron density produced by substituents is given by Hammett's  $\sigma$  (see footnote 8), constants. They are defined as the logarithm of the ratio of the ionization constant of the meta or para substituted benzoic acid to that in the unsubstituted acid. A high positive value of Hammett's  $\sigma$  indicates a decrease in electron density. The fundamental correctness of these concepts may be judged from the results of certain calculations regarding the charge distribution in substituted benzenes [37].

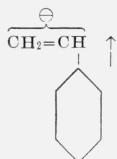
## 2. Induction and Polarization Effects and Relative Reactivities

Reverting now to the problem posed in the beginning, it may be seen that several factors ought to be considered in attempting to account for the relative reactivities obtained and to predict the comparative behavior of monomers toward the same radical. The first ones are the over-all

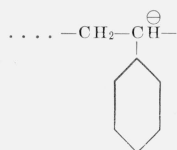
<sup>7</sup> See for instance, G. E. K. Branch and M. Calvin, *The theory of organic chemistry*, (Prentice-Hall, Inc., New York, N. Y., 1941).

<sup>8</sup> See, for instance, L. P. Hammett, *Physical organic chemistry* (McGraw-Hill Publishing Co., Inc., New York, N. Y., 1940).

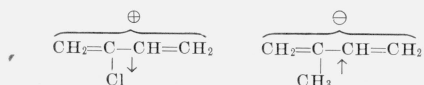
availability of electrons and, perhaps to a lesser extent, the direction of polarization of the double bond. Let us take first the styrene radical as a basis for comparison. In the stable monomer, the double bond should have a relatively high electron density because of the character of the phenyl group as an electron donor as evidenced by the direction of the dipole moment, which is opposite to that in toluene [45]. It should be remarked, however, that Hammett's  $\sigma$  for the phenyl groups is positive. Thus



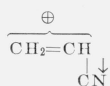
It is reasonable to assume that this over-all negativity carries over to the radical end of a growing vinyl chain [24]:



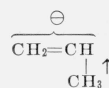
One can then expect that, under otherwise equal conditions (see below) addition to styrene of a monomer in which the inductive effect decreases the over-all availability of electrons in the pertinent double bond is favored in comparison with a monomer in which it is increased. It will be noticed, for instance, in table 3 that out of the three dienes, chloroprene shows the highest activity, isoprene the least and butadiene is intermediate.



Also from tables 3 and 4 it can be seen that acrylonitrile monomer adds preferentially to styrene radical and styrene monomer adds preferentially to acrylonitrile radical because of the opposing effects of the substituent groups. The cyanide group decreases the electronic density.



One would similarly expect propylene to show low activity with styrene.

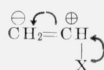


Even allyl chloride has a low reactivity with styrene, as seen in table 3. Contrary to what one might expect by analogous reasoning, methyl methacrylate is slightly more active than methyl acrylate. The difference however, may not be significant.

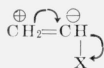
The data on the substituted styrenes [35] in table 3 provide further support for the viewpoint expressed above. They indicate the existence of a correlation between Hammett's  $\sigma$  values for the respective substituent group and the corresponding relative reactivities of the substituted styrene monomers with styrene radical. A high  $\sigma$ -value, which is characteristic, as said before, for a decreased electron availability on other groups attached to the ring is accompanied by greater reactivity. A similar arrangement can be made in respect to the methyl methacrylate radical. Exceptions are encountered with respect to *p*-OCH<sub>3</sub>, and *p*-N(CH<sub>3</sub>)<sub>2</sub>-styrene. The reactivities are higher than would correspond to the position of the substituent on the  $\sigma$ -scale. The authors [35] point out that these compounds are particularly effective in forming complexes with conjugated carbonyl systems. Generally such complexes can be formed by electron transfer between constituents of the complex [36]. In this connection the high selectivity ( $\sigma$  and  $\mu$  very small) of allyl acetate and maleic anhydride is of interest [7]. Here there exists a possibility of resonance structures between radical and monomer which correspond to charge transfer within the activated complex. This possibility appears likely in view of the colors formed by maleic anhydride in mixtures with electron donor-type molecules such as stilbene, indene, and styrene. The difference between maleic anhydride and a quinone-type inhibitor would be a matter of degree and depend on the extent of resonance stabilization of the new radical formed. Inhibition is then effected by the removal of the stable radical through some further side reaction.

The direction and extent of polarization of the double bond can be of importance in favoring

a high reactivity. A monomer such as the one below



should tend to react with a styrene radical by adding head to head, which would bring into play interference by the group X, resulting in decreased activity as compared to the case:



Consideration of the resonance structures in biphenyl (see footnote 8) suggests that the phenyl group should be *o-p*-directing and therefore polarize the double bond in the direction indicated by the first of the above formulas.

The relative stabilities of the radical ends are a second factor governing the propagation rates. The styrene radical is relatively stable because of resonance through the benzene ring. In considering two reactions, the one producing the more stable radical end will be favored. Thus in comparing vinyl acetate with methyl acrylate monomers, the latter will exhibit the greater activity because of conjugation. The inductive effects should be approximately equal in magnitude for these two isomers. Resonance in the styrene radical would be more important than in the acrylate radical. The value for the acrylate monomer is nevertheless slightly larger than unity, probably, because of the direction of the inductive effect away from the double bond. One might expect the formation of acrylonitrile radical to be somewhat favored by the resonance effect. From this point of view all dienes should represent favorable cases.

We have been using for the purpose of illustration almost exclusively the styrene radical because of the wealth of data available. The concepts developed are in fair agreement with experimental results obtained on other radicals. In the case of vinylidene chloride, the radical resonance stabilization can play no significant role. The chloride groups make the monomer positive in the sense previously discussed. Therefore, it shows a high activity, with styrene monomer and a lesser one with methyl methacrylate, which would not be extensively polarized because of the opposing effects of the methyl and methyl substituted carboxyl groups. With the more positively polar-

ized acrylonitrile, the activity is still further reduced. For the same reasons, a similar order of activities is obtained, at least in a qualitative way, for acrylonitrile radical and methyl methacrylate radical with the same monomers. The electrostatic effects of groups on diene radicals should be less important than in their monomers, because the effects would be most important on the double bond, and the group is always one or more bond distances away from the activated end in the case of 1,4-addition. The double bond itself should act as an electron source. Actually the few data available could be interpreted by assuming that the diene radicals are somewhat negative regardless of the character of the substituent. However, the values for acrylonitrile relative to the dienes do not appear to fit this picture.

The mass of data given can be summarized in terms of constants that refer to pairs of radicals and monomers (see table 2). It would be desirable indeed to obtain constants characteristic for each monomer as such. This would in principle allow the prediction of reactivity ratios. The complete realization of such a program seems remote in view of the many factors involved and the probable existence of coupling effects.

### 3. Semiempirical relationships

The preceding discussion makes it evident that the polarity of radical and monomer and the relative stabilities of the radicals are the most important factors to be considered. An attempt to find a set of characteristic numbers in terms of these two effects has been recently made by Alfrey and Price [6]. It is suggested that the various influences are separable and can be represented in the following way:

$$k_{gB}(A) = P_A Q_B \exp(-e_A e_B),$$

where  $k_{gB}(A)$  is the rate of addition of monomer  $B$  to radical  $A$ .  $P_A$  is characteristic for the radical. The  $e$ 's are a measure of the effective charge on the end of the radical taken to be identical with the charge on the double bond of monomer  $A$  and on the double bond of monomer  $B$ , respectively.  $Q_B$  represents a mean reactivity of monomer  $B$  obtained by forming the geometric mean of the reactivities of  $B$  with a series of radicals  $A, B, \dots$  and then assigning to one monomer a reference value of unity. This equation implies that the free energy of activation for the propagation

step is additive in respect to the above-named effects. In comparing the behavior of monomers *A* and *B* toward radical *A*,  $P_A$  cancels out and one obtains for the ratios:

$$\sigma = \frac{k_{rA}(A)}{k_{rB}(A)} = \frac{Q_A}{Q_B} \exp[-e_A(e_A - e_B)] \quad (17)$$

$$\mu = \frac{k_{rB}(B)}{k_{rA}(B)} = \frac{Q_B}{Q_A} \exp[-e_B(e_B - e_A)]$$

$$\sigma\mu = \exp[-(e_A - e_B)^2]. \quad (18)$$

By the use of these equations, a set of relative  $Q$ - and  $e$ -values can be derived from the experimental results. They are presented in table 5 for some typical vinyl monomers. The result for the polarities is in general agreement with the point of view discussed before, styrene being the most negative and acrylonitrile the most positive of the four. The order of the  $Q$ 's show a parallelism to the stabilities expected on the basis of the possible resonance structures for the radicals previously mentioned. Furthermore, the set of values is self-consistent in as much as they give  $\sigma$ 's and  $\mu$ 's that are in agreement with the experimental data on all combinations of these four monomers.

TABLE 5  $Q$ - and  $e$ -values for vinyl compounds

Monomer	$Q$	$e$
Styrene.....	1.00	-1
Methyl methacrylate.....	.64	0
Acrylonitrile.....	.34	+1
Vinylidene chloride.....	.16	0

Some difficulties arise if one attempts to fit the other olefins studied into the framework represented by table 5. The  $Q$ -values are not always consistent with the interpretation given to them and neither are the polarities. No satisfactory results are obtained by applying eq 17 and 18 to the data on dienes obtained by Henery-Logan and Nicholls (see footnote 5). In deriving these results the equality of effective charges for monomer and radical is assumed. As mentioned previously, it seems to us that in the case of dienes a differentiation ought to be made particularly when the inductive effect of a substituent acts to decrease the electron availability [32]. On this basis one can evaluate the pertinent data in conjunction with the values for the vinyl compounds

given in table 5. We modify the two eq 17 and 18 by replacing the first factors  $e_A$  and  $e_B$  by  $e_A^*$  and  $e_B^*$  and one factor  $(e_A - e_B)$  in eq 18 by  $(e_A^* - e_B^*)$ , respectively. The star refers to the radical. The result of these calculations is summarized in table 6. The differences in sign between the  $e$ -values are in the expected direction. All  $e^*$ -numbers are negative, the one for chloroprene being the least. The few data available for an independent check are rather well reproduced by using table 6. It can be seen from eq 17 that a large value of the ratio  $Q_A/Q_B$  for a set of  $e$ 's corresponds to large values of  $\sigma$  and small values of  $\mu$ . Thus monomers with great disparity in the  $Q$ 's, will copolymerize poorly. Large differences in the  $e$ 's, of course, lead to good copolymerization.

TABLE 6.  $Q$ ,  $e$ , and  $e^*$  for dienes

Monomer	$Q$	$e$	$e^*$
Chloroprene.....	2.2	0.9	-0.6
Butadiene.....	2.5	-1.4	-1.2
Isoprene.....	3.5	-1.4	-1.3

#### 4. Steric Effects

In considering the copolymerization of compounds such as stilbene, indene, maleic anhydride, the maleates, and the fumarates, another factor becomes important, namely steric hindrance. For example, the symmetrical substitution of another phenyl group in styrene leads to a compound, stilbene, which does not polymerize. Maleic anhydride and other symmetrical disubstituted ethylene derivatives polymerize with difficulty, if at all. However, stilbene and maleic anhydride form copolymers. The hindrance in such a case should still be great but is apparently overcome by the influence of polarity effects since the pertinent double bond can be expected to be positive in maleic anhydride and negative in stilbene.

A striking example of steric hindrance is provided by the comparison of maleic anhydride, diethyl chloromaleate, and diethyl maleate [4, 5]. The reactivities with styrene radical are respectively 24, 0.4, and 0.2. These differences have been ascribed to the opening of the anhydride ring [24]. Diethyl fumarate has a reactivity of 2.5 toward styrene monomer [24]. The increase over that of its *cis*-isomer can be understood on the

basis of the geometry of the two molecules, if the respective resonance structures of maleates and fumarates are considered.

The preceding discussion dealt entirely with relative rates of propagation in copolymerization, which are the ones determining average composition. Differences between monomers are, of course, to be expected in respect to the other steps of the chain reaction. In considering for instance, the rate of peroxide induced initiation, the polarities of monomer and catalyst radical and the stabilities of the radicals formed are of importance. We would expect the phenyl and the benzoyl radicals to be negative. It is not possible to compare directly the rates of initiation in two binary systems, since the rate of decomposition of the peroxide depends markedly on the medium [22]. This can be minimized by using dilute solutions of the monomers in an identical solvent. It serves no purpose to discuss in any greater detail possible effects of monomer structure on the relative rates of elementary acts other than propagation, until a complete kinetic analysis of the copolymerization of at least some typical pairs has been obtained.

### 5. Effect of Intramolecular Arrangement on Degradation

The whole discussion has hitherto referred to the building up of copolymer chains. It is of interest to consider also the reverse process. It is not our purpose here to discuss in detail thermal decomposition of polymers. We merely wish to point out briefly the relationship between the structure of the copolymer as considered previously and the results to be expected in its degradation. Studies of the thermal decomposition of various copolymers have shown that in many cases the yield of monomers are much lower than what would be expected from the number of monomer units known to be in the polymer and the behavior of the simple polymer [33]. For example, the yield of styrene from GR-S is much less than the corresponding yield of styrene from polystyrene.

Assuming that the effect of side reactions on the yield of a given monomer remains constant in going from simple polymer to copolymer depolymerizations, the pyrolysis yield of certain types of monomers obtained from a copolymer of given composition may be calculated. Let  $A$  represent monomers of the mono or asymmetrical disubsti-

tuted ethylene type ( $\text{CH}_2\text{CXY}$ ) with head-to-tail arrangement in the simple chain and in the copolymer, and  $B$  monomers of the diene of symmetrically disubstituted ethylene types. In comparing the expected yield of  $A$  from a copolymer with the corresponding one from a pure polymer  $A$ , we proceed in the following manner. Consider a sequence of  $i$   $A$ -units, which in the case of the copolymer is bounded by  $B$  units. There are  $2i$  possibilities of producing a split,  $2i-1$  in the interior and  $2 \times \frac{1}{2}$  at the boundaries, where the factor  $\frac{1}{2}$  is included to avoid twofold counting of the bonds joining the sequence to the rest of the chain.  $2i-1$  of these splits produce monomer  $A$ . If the probability of occurrence of a sequence of length  $i$  is denoted by  $P_i(A)$  (eq 15), the yield  $Y_c$  of  $A$  from the copolymer becomes equal to:

$$Y_c = Y_0 \sum_{i=1}^{\infty} \frac{2i-1}{2i} P_i(A), \quad (19)$$

where  $Y_0$  denotes the expected yield of monomer from the pure polymer  $A$ . In deriving eq 19, it has been assumed that splitting occurs at random and independent of the nature of the adjacent units in the chain. Also recombination is excluded. One would expect large positive deviations from the calculated yields to be an indication of head-to-head and tail-to-tail structures in the polymer. For in such a case, the effect of the sequence boundaries considered in eq 19 is absent. In practice, the number of such configurations is usually small and obscured by other factors. Using the expressions (eq 15 and 16), we finally obtain from eq 19:

$$\frac{Y_c}{Y_0} = \frac{A}{A + \mu B} \left[ 1 + \frac{B}{2\sigma A} \ln \frac{B}{\sigma A + B} \right]. \quad (19a)$$

Since the composition of the copolymer can be determined from eq 4a, the thermal decomposition yield can be plotted against the instantaneous polymer composition as shown in figure 15 for the styrene-butadiene system using the pertinent values of  $\sigma$  and  $\mu$ . For certain copolymers, such as the polybutenes, where the monomers are isomers or otherwise similar, this may be a useful tool for the development of a pyrolytic analytical technique, particularly since most monomers can be determined spectrometrically, while the copolymers cannot always be analyzed. The full application of this technique



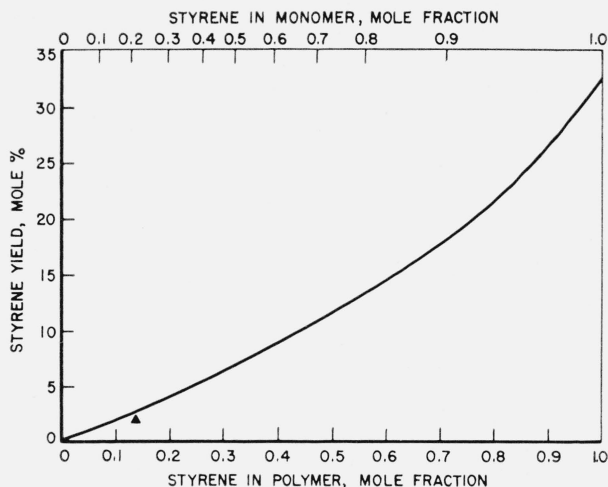


FIGURE 15. Theoretical yield of styrene from butadiene-styrene copolymer as function of instantaneous polymer composition.

▲, Experimental for GR-S.

will require precise control of pyrolysis conditions and highly refined analytical methods. At present, the above concepts will account for some of the results found in the depolymerization of copolymers.

## 6. Conclusion

In conclusion, the obvious main lines for further work may be sketched. Kinetic studies on copolymers are few and will have to be extended to include over-all rates, and at least in some typical cases, determinations of the individual rate constants of the chain reaction. It will be further interesting to see whether the observed reactivity ratios can be related to the structure of the monomer through other constants characteristic of the same. Consideration of dipole moments, polarizabilities, and ionization potentials may offer some clues. Indications as to steric influences in the copolymer chain may be gained by a comparison of the heats of reaction of the pure and mixed species.<sup>9</sup> The preceding discussion dealt primarily with the mechanism of formation and the resulting structure of the copolymer. Apart from the work on GR-S, no systematic studies of the relation between these factors and the thermodynamic [26] and rate properties of copolymer solutions seem to have been undertaken. Some physical properties of

certain copolymers besides synthetic rubbers have been systematically investigated.<sup>10</sup>

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<sup>9</sup> See in this connection a remark made by M. G. Evans, *J. Chem. Soc.*, **1947**, 264. L. K. J. Tong and W. O. Kenyon, 113th meeting of the American Chemical Society, Chicago, Ill., April 19 to 23, 1948.

<sup>10</sup> See, for instance, W. O. Baker, in *Advancing fronts in chemistry 1*, High polymers (Reinhold Publishing Corp., New York, N. Y., 1945).



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